

THEORY OF PARTICULATE PROCESSES

Analysis and Techniques of Continuous Crystallization

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*To our wives, Peggy and Ruth,
for their patience and encouragement*

PREFACE

The need for this book has arisen from the burst of research activity over the last ten years in the area of industrial crystallization from solution. This work began with the first attempts to rationalize, model, and predict crystal-size distributions (CSD) from realistic mixed-magma crystallizers and was based on the concept of a population balance of crystal particles along the particle-size axis. The scope of this general attack on the CSD problem was quickly enlarged to include three main areas of research which have seen much attention during the last decade. These areas, introduced, motivated, and sometimes necessitated by the original CSD studies, are listed below:

Use of the population balance to predict CSD in various crystallizer process configurations with assumed crystal kinetics. This work included studies of fines removal, staging, product classification, and CSD instability as well as the inherent CSD effects to be expected of various crystallization kinetics, e.g., size-dependent growth rates and magma influenced (secondary) nucleation.

Use of the idealized mixed-suspension, mixed-product-removal (MSMPR) crystallizer at the bench-scale, pilotplant, and industrial levels to assemble nucleation and growth rate kinetics correlations in realistic mixed-magma suspensions. This work, performed in both industrial and university laboratories, led to the realization of the importance of secondary nucleation mechanisms in continuous mixed-magma crystallizers and the assembly of large amounts of nucleation-growth rate data which could be adequately correlated with simple exponential (power-law) kinetic expressions.

Extension of the simple size-axis population balance to a generalized continuity equation in particle phase space which can serve as the analytical framework for studies of population dynamics in other particle processes, e.g., comminution, microbial distributions, and dispersed phase extraction systems constituting a formalized theory of multivariate distributions in particulate systems. This is not to say that population balances were not used, in fact were not the framework, in such studies; however, the CSD problem yielded perhaps the most fruitful applications of this population balance theory (undoubtedly because of the simple, but useful, closed-form solutions, e.g., MSMPR model) and thus it was in this context that the full formalism of the population balance in particle phase space was developed.

The fortuitous circumstance of their initial collaboration in 1960 enabled the authors to be a part of this rapid burst of activity from its beginnings. This book is a natural summary of the work over the past decade on CSD in which the authors have participated or are intimately aware.

The main purposes of this book are to present the work on CSD as a more or less complete topic, introduce the reader to the complex subject of secondary nucleation and growth mechanisms which are only now being unfolded, and to present the generalization from CSD studies as a unified predictive theory of particulate systems. No attempt is made at a comprehensive treatment of work other than CSD studies, yet it is hoped that details in the treatment of crystallization processes will be of value to researchers in other areas.

The material in this book has been used as lecture notes for a graduate level special topics course in particulate systems. The material for this graduate course was presented in approximately the same order and level of comprehension as in the book and was supplemented by individual studies from the current literature. Representative particle distribution problems from appropriate chapters are presented in Appendix C. These problems plus the broad, but elementary, attention given to systems other than crystallization should make this book a worthwhile text for use in such graduate level special topics courses as well as to reinforce the researchers' understanding of the material.

It is hoped that the student and researcher alike will not be overwhelmed by the attention paid to crystallization systems but will use this theory as a helpful and logical organization in the understanding of particulate processes.

ACKNOWLEDGMENTS

The writers are deeply indebted to their colleagues who have contributed so much to the work presented in this book. Certainly all of the excellent work that has been done on the CSD problem is not cited in text, however a more complete bibliography of recent work in the study of particulate distributions is given in Appendix D. The bibliography is not claimed to be exhaustive and the authors apologize for any major omissions which have occurred.

The authors acknowledge the outstanding efforts of their graduate students of the past few years who have materially advanced knowledge and understanding of this area. In particular, ADR wishes to thank Messrs. Krisnaswami Rajagopal, Paul D. Stone, Chand Deepak and Magdi Iskander, his graduate students at the University of Florida, and Messrs. Michael D. Cise, Rufus Crawford, Antonio R. Durando, and Herbert E. Nuttall, his graduate students at the University of Arizona. MAL wishes to acknowledge the contributions of Messrs. Donald C. Murray, Delmar C. Timm, Carroll W. Chambliss, Ashok B. Amin, Philip R. Wolff, Wayne J. Genck, Steven M. Shor, George W. Becker, Jr. and Janardhana B. Baliga, his graduate students at Iowa State University and also the contributions of his colleague Professor John D. Stevens and his graduate student Mr. Carl Abegg.

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Finally, the authors would like to acknowledge the influence of Professor Ray W. Fahien, as a teacher and colleague, on the authors' formal education, technical philosophy, and career outlook. The many influences of Ray Fahien as a teacher, scholar, and friend may be seen throughout this book.

INTRODUCTION

1.1 Particle-Size Distribution

The solid state of matter is unique in that it exhibits properties related to form and state of subdivision as well as to extent and composition. For example, ball bearings are useful in a specific application because, first, they are round, and second, they are a certain size. We take this for granted with individually manufactured items; it is less obvious but equally true for solid materials produced in the bulk. Further, bulk-manufactured solid materials owe their characteristic shapes and sizes to the processes which produced them, and because these processes are often secondary, perhaps even completely random, in their action on the particles, there results a distribution of sizes and shapes of the resultant solid-phase material. If all particles are roughly similar in their appearance (shape), it is often adequate to describe the material with a one-dimensional particle-size distribution. Chapter 2 discusses several empirical, one-dimensional distribution functions suitable for such use, while Chapter 3 presents a unified theory for multidimensional particle distributions which can be used to analyze and predict such distributions in certain regular, well-defined processes. Chapter 3 suggests a generalization of particle "size" as any one of the particle's internal coordinates. The *internal* coordinates of a particle distribution are the least number of independent properties associated with a particle distribution, excluding its position dependence, which completely specify all measurable properties of the distribution. Examples, in

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addition to the actual size of the particles, would be their age in an environment, their catalytic activity (for the case of a suspension of catalyst particles), their chemical composition (for the case of liquid extraction in a dispersed-phase liquid-liquid extraction process), and the biological properties of a microbial distribution. Thus, when two or more of these internal coordinate properties vary from member to member in the population, a multidimensional distribution function is necessary to completely specify the system. These internal coordinates, combined with the external (spatial) coordinates of the particles, comprise the particle phase space of the distribution.

The adequate definition and measurement of particle size in the conventional sense for a sample of particulates is a difficult matter at best, especially when the particles have odd and varying shapes. A particle may be thought of as the size element of matter which best describes the state of subdivision of the material and has a shape characteristic of the processes and forces producing the particles. With this particle definition, particle size must then be the linear dimension which best characterizes the state of subdivision of the material within the context of the typical shape of the particles. A characteristic dimension of a particle can be thought of as a line passing through the center of mass of the particle and intersecting two opposing surfaces. Figure 1.1-1

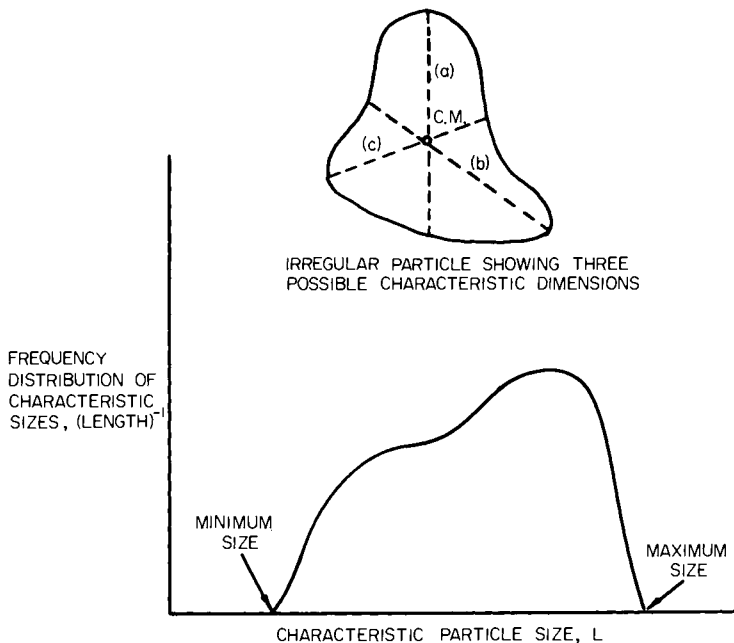


Fig. 1.1-1 Variation in characteristic particle size for an irregular particle.

sketches an irregular particle with three such characteristic sizes drawn through its center of mass. For highly irregular particles, such characteristic sizes are infinite in number and themselves can be represented by a one-dimensional frequency distribution as also shown in Fig. 1.1-1. Fortunately, this variation in characterization of individual particle size is averaged when a size distribution is obtained on a sample containing a large number of particles. The actual size that is measured in a particle-size distribution analysis lies between the minimum and maximum characteristic sizes shown in Fig. 1.1-1, and depends on the method of measurement. A comprehensive discussion of the definitions and techniques of particle-size measurement is outside the scope of this book.¹

1.2 Crystal-Size Distribution

Most of the examples in this book refer to crystallization applications of the theory of particulate systems, because of the particular background of the authors; however, this theory can be broadly applied to many other systems. Certainly crystallization is a very ordered, if complex, process and much effort has been devoted in the past few years attacking the crystal-size distribution (CSD) problem in its many aspects. This book draws generously on these earlier efforts. The generalization of CSD theory to that of a unified theory of multidimensional distributions in particulate processes is valid, however, and it is hoped that the reader interested in other particulate processes will not be overwhelmed by the attention devoted to crystallization.

Crystal-size distribution is one of the most important, difficult to predict, and least understood properties of crystallization processes. CSD is an important property affecting the end uses of the crystalline product as well as interacting strongly with the crystallization process itself.

Some of the more important problems in the operation of industrial crystallizers involve (a) crystal-size distribution, (b) crystal habit and purity, (c) salting (fouling), (d) capacity and scale-up, and (e) crystallizer stability. All of these problems interact strongly with the CSD being produced and, in fact, most of these problems could be listed as subheadings under the CSD problem. The main mechanism of interaction of these problems with CSD is through the level of driving forces (supersaturation) in the process. Crystallization is an area-dependent process and thus the driving forces necessary for a given rate of crystal production are inversely proportional to the crystal area available for deposition.

¹ For an excellent discussion of particle definitions and size measurement techniques, see Irani and Callis [1].

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Supersaturation levels can alter the habit and/or purity of the product crystals. Habit changes can come about by changing the relative growth rates along the crystal axes, thus changing the length-to-width ratio and basic shape of the crystals, or habit changes can result from surface nucleation and/or twinning, which results in multicrystal growth, producing very irregular crystals. Crystal purity has a very complex interaction with supersaturation, and hence CSD, due to either impurities on a molecular level resulting from the altering of the mechanisms of molecular growth rate or gross impurities resulting from occlusions. In every case, to understand the problems of habit and purity, it is necessary to come to grips with the CSD problem.

Fouling of surfaces in a crystallizer is obviously affected by the level of supersaturation and hence by the CSD. Such fouling necessitates shutdown for washout and such washouts represent one of the major operating problems of industrial crystallizers. Often, there is a tradeoff between a more desirable CSD produced with higher driving forces versus the increased washout frequency with such operation. The theory of CSD developed in this book is directly applicable to the analysis of the maximum driving forces occurring in a crystallization process and hence to a logical attack on prediction of salting conditions.

Scale-up of crystallization processes from bench-scale to pilot-size to industrial-size is a difficult problem and again relates to the CSD problem. In general, if the intensive properties of an element of mixed crystal magma remain invariant upon scale-up, CSD will remain invariant. However, supersaturation generation, flow patterns, degree of mixedness, and factors affecting secondary nucleation do not remain invariant with a change in scale of the process. For example, supersaturation is produced in a two-dimensional manner through vaporization at a boiling surface or cooling across a surface exchanger, while the volume of a crystallizer scales in a three-dimensional manner. Thus, as the size of a crystallizer increases, assuming constant magma circulation velocities, an element of fluid at the zone of supersaturation creation must circulate a longer time before reaching the extremities of the crystallizer. Therefore, constant properties in this element of magma cannot be maintained and changes of CSD with scale-up occur. The art of CSD scale-up involves understanding the factors resulting in a given CSD at each level of operation and then predicting the magnitude of these factors and the resulting CSD in the desired full-scale operation.

Stability of operation is directly related to CSD. The transients of CSD are characterized by long lag times. Typical upsets consist in idling the discharge, water addition, temperature excursions during washouts, temporarily stopping feeds, and recycling or accelerated removal of crystal magma. Hydraulically speaking, the crystallizer, having a large retention time, is quite stable to such process interruptions; however, CSD may be profoundly influenced by such

upsets and during the long recovery time of CSD, during which time hydraulic and temperature upsets have long since stabilized, there is a great temptation to make further operating changes which again affect CSD. Excursions in dilution and/or temperature of a crystallizer can have a pronounced effect on CSD because of changes in the nucleation rate. Such upsets require a maximum recovery time to return to a stable CSD.

Furthermore, the process of crystallization has a unique internal process information feedback loop which regulates the CSD produced. The mechanism for this information feedback is through the level of driving forces (supersaturation) resulting from the rate of production and the total crystal surface area available for deposition. The supersaturation level determines the rates of nucleation and growth, which in turn determine the dynamic CSD at any given time. Similarly to classic instrument feedback control systems, if the amount of system gain is excessive, the process exhibits erratic behavior and may become unstable. The CSD information feedback in a crystallizer increases as the relative sensitivity of nucleation rate to growth rate increases for a given variation in supersaturation, and thus CSD dynamics and stability become a function of nucleation-growth rate kinetics. It can be theoretically shown that a crystallizer can be operated in a kinetic regime where it becomes a chemical oscillator, i.e., it exhibits sustained limit-cycles of CSD, ranging between a coarse and a fine product. These cycles are sustained without any process upsets. Large-scale industrial crystallizers have been observed to operate with such CSD limit-cycles. CSD transients and stability will be discussed in detail in Chapter 5 using the theory of particulate processes developed in this book.

Even if CSD had no interaction whatsoever with the operation of crystallization processes, CSD would still be one of the most important characteristics of a crystallization process because CSD largely determines the end use of the crystalline product. One of the strongest examples of this interaction of CSD with end use is in the handling and marketing of crystalline fertilizer products (Fig. 1.2-1). A few of these problems are those involving caking in storage, dusting and breakage on handling, and segregation after blending.

Fundamental studies of the caking mechanism indicate that caking is certain when the ambient humidity cycles about the vapor pressure of a saturated solution of the crystalline material, i.e., caking is directly related to the formation and dehydration of a saturated liquid film on the crystal surface. Such caking in the open-air bulk handling of fertilizer products is thus unavoidable, but the severity of the problem depends to a large extent on the absolute size and size distribution of the crystal product. Very small crystals having a large specific surface area and crystals with a wide CSD resulting in a dense packing of the smaller crystals in the interstices between the larger ones both result in severe caking problems.

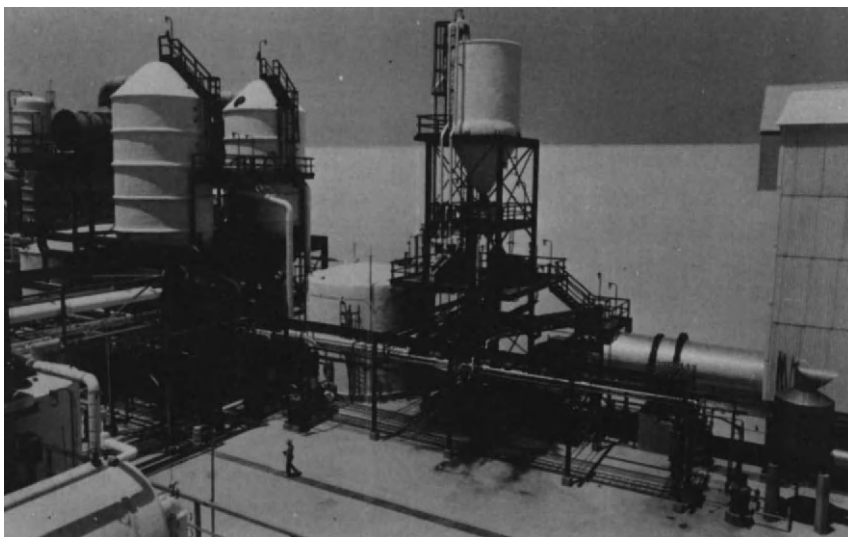


Fig. 1.2-1 Potash crystallizers in operation at the Dead Sea Potash Works, Israel (courtesy Swenson Division of Whiting Corporation). Crystal-size distribution is an important factor in the operation of such processes as well as in the use of the fertilizer product.

Dusting is a result of both the amount of fines produced with the original CSD and the subsequent size degeneration resulting from poor crystal habit. Dusting from a crystalline product results in material losses and is a nuisance problem to personnel handling the material.

No single crystalline fertilizer is ideal for all applications and it is common practice to produce blended granular fertilizer mixtures. Segregation and/or uneven application occurs when the CSD's of each of the components are not suitably compatible. Transportation of the blended mixture long distances in bulk containers can result in a dramatic segregation of the component crystals.

These problems of fertilizer handling and end use may appear trivial at first glance, yet the ability of a manufacturer to compete in the near-commodity fertilizer market often hinges on his ability to cope with these CSD-related problems.

The appearance of a granular material is grossly affected by its size distribution. Ordinary table sugar and salt are two commodities whose acceptance by the housewife is largely related to their appearance of uniformity and hence their size and size distribution. A narrow particle-size distribution, indicated by a low coefficient of variation (standard deviation of particle size divided by mean particle size) appears much more homogeneous than distributions with a large coefficient of variation. This is illustrated by Fig. 1.2-2, which shows photomicrographs of $(\text{NH}_4)_2\text{SO}_4$ crystals with approximately the same mean

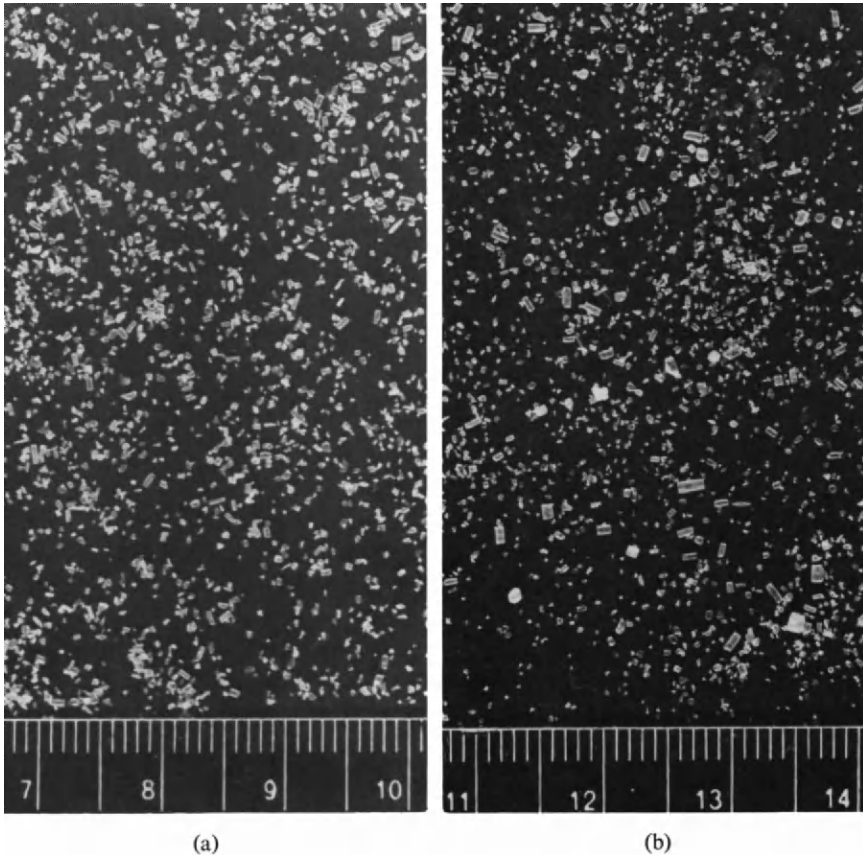


Fig. 1.2-2 Photomicrographs of $(\text{NH}_4)_2\text{SO}_4$ crystals having mean size of $300\ \mu\text{m}$ with a coefficient of variation (a) 0.25, (b) 0.6.

but with coefficient of variation (weight basis) of (a) 0.25 and (b) 0.60. The appearance of uniformity (visual) is a function of absolute sizes as well as of the width of the distribution and a few very large particles can give an otherwise uniform distribution a very heterogeneous appearance. If esthetic visual appeal is an important market factor, this fact often necessitates scalping of the oversize from the product crystals.

1.3 Comminution Processes

Comminution processes represent a second example in which the resultant size and size distribution of the particulates are the most important properties

affected by the process. Crystalline mixtures are often ground to the desired end-use size and such operations are important in the basic chemical industry, but by far the largest comminution processes (certainly tonnage-wise) occur in the mineral industry. As a specific example, the lowest grade of copper ore that can be economically processed in the United States is somewhat lower than 0.5% copper. Thus, roughly 200 tons of ore must be crushed and ground to a fine state of subdivision to liberate one ton of copper values. In a typical sulfide ore, calcacite, copper values of the mineral calcacite are widely dispersed in the rock matrix and grinding to below 100 mesh is necessary to effectively liberate the copper values. Concentration of the copper ore is accomplished by flotation and the grind must not be too fine, to avoid excessive slimes, power consumption, and flotation reagent usage.

In order to achieve a degree of uniformity in the ground ore, grinding mills are often operated in closed circuit, i.e., with a recycle of oversized particles, as shown in Fig. 1.3-1. The equipment sizes and tonnages handled in the mineral industry often dwarf other large-scale basic chemical processes. Figure 1.3-2 shows the layout of a modern ball mill grinding circuit in operation in the copper industry.

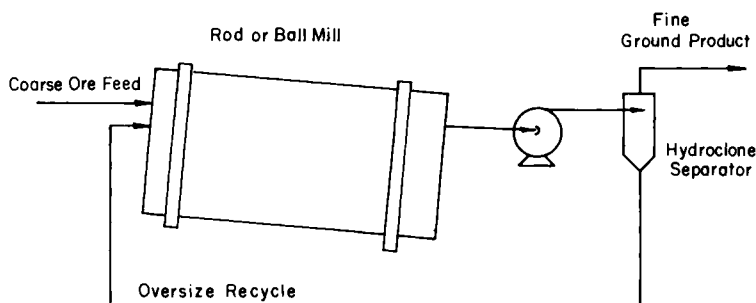


Fig. 1.3-1 Schematic diagram of closed-circuit grinding mill (Preprint 71-B-78 presented at AIME Meeting, New York, March 3, 1971).

There is considerable economic incentive for proper understanding, operation, and control of such large-scale grinding processes as are found in the mineral industry. From Fig. 1.3-1, it can be seen that total mill throughput is directly related to the ability to grind down to proper size; the oversize will be recycled, with a subsequent reduction in primary feed rate to keep total mill solids content in balance. A realistic understanding of the size distribution performance of such a unit involves an understanding of the oversize classifier as well as the grinding mill itself. Information regarding the current particle-size distribution performance of a closed-circuit grinding mill can be fed back for control of size distribution or fed forward to obtain optimum operation of

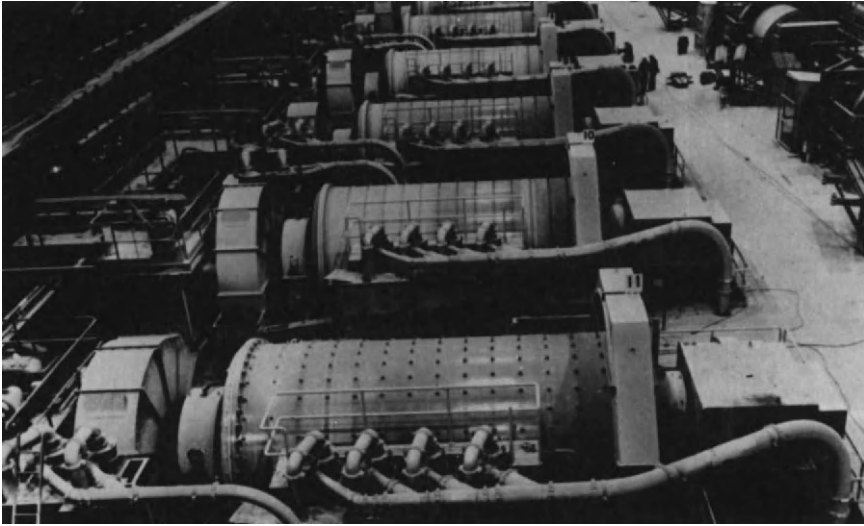


Fig. 1.3-2 Grinding circuit layout in modern size-reduction mill. (Anaconda's Butte copper mine, Butte, Montana. Courtesy of the Anaconda Corporation.)

subsequent ore concentration in flotation cells. Thus, there is a great need for the ability to predict size distribution by simulation of such a system and also to experimentally obtain on-line measures of size distribution performance.

Much effort has been expended in the recent literature to formulate reasonable empirical models of a grinding mill. Most of this empiricism centers around a determination of the so-called selection and breakage matrices. These matrices partition, on a weight basis, the fraction of particles at a size breaking per unit time as well as the fraction of the pieces going to a given size range below the original broken particles. As the selection and breakage matrixes are of order N , where N represents the number of size increments to be represented, this empiricism, although simple in theory, is difficult to grasp in practice. The particle-size distribution theory presented in this book gives an alternate approach to this problem wherein the empiricism is inserted in population balances in the particle phase plane. The resultant equations, still dependent on correct empiricism, are perhaps more formidable in appearance but the empiricism is in the form of continuous functions and is easier to grasp. Transient and spatial distribution of the particle-size distribution are "built in" to the particle phase space and thus simulation at any level of sophistication can be obtained.

Examples of comminution size-distribution simulation using the population balance theory of particulate processes developed in this book will be considered in detail in Chapter 10.

1.4 Other Particulate Processes

Although this book concentrates almost exclusively on the process of crystallization for its descriptive examples, there are many other examples of particulate processes besides comminution processes as described above, where the theory presented here could be and has been applied to obtain quantitative descriptions of the particle-size distributions produced in the process.

Continuous microbial processes produce distributions of cell cultures which can be quantitatively described with a mathematical structure very similar to CSD in a crystallization process. Such cell populations can be distributed about one or more independent internal coordinate dimensions as well as distributed in time and space, thus demanding, and in fact contributing to, the full formalism of multidimensional particle distribution theory. The chief problem in the description of complex microbial distributions consists in obtaining an *a priori* quantitative description of cell dynamics rather than in the quantitative description of residence-time distributions (process flows) imposed on the process. Such continuous microbial processes are certain to be of increasing importance in the future and will require a great deal of co-operation between the biologist and chemical engineer for their quantitative description.

The population-balance-derived continuous theory of particle-size distribution can and has been applied to the problem of predicting the interaction of process flows with chemical kinetics to produce polymer chain lengths of various molecular weight distributions. Again, the problem is not that of quantifying the process flow distribution, but is that of specifying quantitative *a priori* kinetic models as a function of the state of the system for the various molecular initiation and termination mechanisms. Molecular weight distributions in polymer solutions are simulated with the continuum theory of particulate systems by representing growth by monomer addition as a continuous linear growth rate while chain additions and active site initiation and termination are represented by kinetic birth and death functions of the entire distribution in the system; in general, phrasing birth and death functions in terms of the entire distribution results in a set of integrodifferential describing equations.

Liquid-liquid extraction from a disperse-phase droplet suspension is an example of a particulate system requiring two internal coordinates to completely specify the mass transfer occurring. These coordinates are the droplet size distribution, giving the total interfacial area available for mass transfer, and the distribution of solute concentration in the droplet phase, itself a complex function of the rate of mass transfer and the coalescence and re-dispersion forces creating and maintaining the droplet suspension. The major obstacle to be overcome in utilizing the particulate systems theory of this book

is to generalize on the form of the droplet coalescence and redistribution death and birth terms as a function of the basic hydrodynamics of the system. Again, these terms are normally phrased as functions of integrals of the entire distribution, with the resultant complexity of integrodifferential describing equations.

Other examples of particulate processes capable of quantitative description with this population-balance-derived theory of particulate systems are the particle-size distributions of solids in metallized-propellant rocket-engine exhausts, droplet formation and precipitation in weather modification studies, and biological and/or demographic studies.

If all of the possible particulate processes capable of quantitative study are set alongside the problem of prediction of CSD in crystallization processes, it becomes obvious why most of the previous work centers around CSD studies. The CSD-describing equations are notable by the normal absence of the birth and death functions, i.e., in most well-designed crystallization systems, the change of CSD form due to crystal fracture can be neglected and the crystals are predicted to travel along continuous trajectories in particle phase space due only to convective flow (molecular growth). Other particulate processes, i.e., comminution, polymerization, microbial, etc., are characterized by the dominance of the birth and death functions. This results in a second level of empiricism as well as in difficulty of solution of the resulting equations. Simple analytic solutions are absent from which empirical kinetics can be unambiguously deduced. It is felt that progress in the *a priori* study and prediction of particle-size distributions other than CSD will be hindered until direct observation and correlation of the birth and death terms for net particle generation at a point in particle phase space become a practical reality.

Reference

1. R. R. Irani and C. F. Callis, "Particle Size: Measurement, Interpretation, and Application." Wiley, New York, 1963.

PARTICLE DISTRIBUTIONS

2.1 Introduction

Particulate dispersed-phase systems are inherently more difficult to describe than systems comprised of one or more bulk phases. Whereas temperature and composition, together with rate or equilibrium relationships, are often sufficient to characterize the latter systems, additional information is often needed, and in fact, is vital in characterizing particulate systems. Such additional information arises from the fact that one or more independent properties can be given values for each individual particle entity in the dispersed system. For example, consider droplets of one phase dispersed in a second, immiscible phase, with mass transfer of a third, dilute component occurring across the droplet interface. For each droplet, we can assign a value for its size and a value for the average concentration of the component being transferred. Thus, particle size and particle concentration are two independent property coordinates which can be given values at any time for each member in the system. A droplet can change in size by molecular additions or subtractions due to equilibrium changes in the amounts of the two immiscible phases or disappear as an entity by coalescence or redispersion, while particle concentration in a drop changes as mass transfer occurs. It is precisely these changes in the internal coordinate properties of the droplets that we wish to describe.

However, not all droplets are of the same size nor of the same concentration. Thus, there is a distribution of sizes and a distribution of concentrations of the

liquid droplets. In practice, it is usually not the coordinate property values of any one droplet which are of interest, but the entire distribution of values. Thus, the discrete particles in the system, with their individual coordinate values, are thought of as a continuous distribution. This continuous distribution may be represented analytically or empirically by a variety of graphical plots. This continuum approach to an inherently discrete system is quite justified when a large number of members are contained in any discrete sampling range of the particular coordinate property of interest.

Once a distribution function for a particulate system is obtained, all the properties of interest regarding the particulate phase are, in principle, known. Often, all that is required in an engineering problem is that some average property of the particulate phase be known. The distribution function can be readily integrated to obtain such averages.

The above two points regarding the continuum assumption and averages over the entire distribution point up some very practical considerations regarding sample size when experimental sampling of a distribution is to be done. The sample size (finite increment of the coordinate property) must be small enough so that, in fact, a point on the distribution curve is obtained, rather than the average, but large enough so that the number of members in the increment is significant. As an example of this point, consider the screening of a granular product which has been formulated by mixing 5 gm of $-100 + 120$ mesh material with 5 gm of $-140 + 170$ mesh material. Assume a deck of 60, 100, and 170 mesh screens is used for analysis. All of the product reports to the 170 mesh screen, and all that can be said is that the material ranges from 88 to $149\ \mu\text{m}$ in size. If the full $4\sqrt{2}$ range of screens is used, the material is seen to lie in the two size ranges, $-100 + 120$ and $-140 + 170$ mesh. If, on the other hand, the particles are divided into smaller and smaller size ranges, say by individual measurement under the microscope, there will eventually be a size range small enough so that either one or no particles are in that size range. At this point, indeed before this point, the continuum assumption breaks down and the discrete nature of the distribution becomes evident.

So far, two examples of property coordinates associated with individual members of a distribution have been mentioned. These were size and concentration distribution of droplets in a two-phase liquid suspension and size distribution of a granular material. These are, respectively, two and one-dimensional distributions. It is evident that one may generalize on the concept of size and say that a "size" distribution of a particulate system is a multi-dimensional distribution of the members of the system about their respective independent coordinate property axes. Complete information is known about the system when all of the coordinate properties necessary to characterize the system are included as independent variables in the distribution function.

It should be noted that the coordinate properties must be independent in

order to completely specify the system with a minimum number of variables. In the previous example, the weight of the individual droplets could be specified as a third coordinate property. However, the weight of each droplet is a unique function of its size and concentration, and thus, droplet weight is a dependent variable and could not be used together with size and concentration to specify the distribution. Any two of the three variables weight, size, and concentration could be used as independent coordinate properties, and a two dimensional distribution about these axes would uniquely specify the system.

One of the two examples chosen illustrates another property which sometimes is associated with a distribution, namely its spatial concentration. In the case of the two-phase suspension, the droplets were distributed, uniformly in this case, in the continuous phase. In a poorly mixed system, we need to consider the distribution in space of the droplets in order to completely characterize such a system. In the case of the granular solid, spatial concentration has no meaning, and the material can be characterized by a single dimension, namely particle size.

It is convenient to refer separately to the two types of coordinate axes as discussed above. Thus, we define:

- a. Internal coordinate properties: properties associated with the internal state of the particle, e.g., size, concentration, chemical activity, temperature, etc.
- b. External coordinates: x, y, z spatial coordinates giving the location of the particle.

The combined internal and external coordinate region is referred to as the particle phase space. In general, given m independent internal coordinates, particle phase space is an $(m + 3)$ -dimensional space, and an $(m + 3)$ -dimensional distribution is required to completely characterize the particulate phase.

2.2 Representation of Distributions

A variety of empirical forms exist for expressing a one-dimensional distribution about a coordinate axis. Such functions may represent the distribution of members of a population having the respective values of the independent property coordinate, i.e., a population distribution, or the distribution function may represent the occurrence of some other dependent property of the population as it is distributed about the independent coordinate axis. These two distribution functions are, of course, closely related to each other, and can, in general, be transformed from one to the other. An example is the particle-size distribution of a granular material. Such a size distribution can be expressed as population versus size or weight versus size. For geometrically similar

particles, particle weight is proportional to particle size cubed, and thus, the weight distribution can be obtained from the population distribution by multiplying by size cubed.

The most widely known one-dimensional distribution function is the normal distribution given as

$$f(L) = [1/\sigma(2\pi)^{1/2}] \exp[-(L-\bar{L})^2/2\sigma^2] \quad (2.2-1)$$

Several properties of this distribution deserve mention. This distribution has two adjustable parameters, σ and $\bar{L}$, which are, respectively, the arithmetic standard deviation and the mean, and are a measure of the uniformity and absolute size of the members of the population. It is obvious from the squared argument in the exponent that this function is symmetric about the mean, $L = \bar{L}$. Further, the distribution is normalized such that $\int_{-\infty}^{\infty} f(L) dL = 1$. The standard deviation is also defined in terms of the distribution function as

$$\sigma^2 \equiv \int_{-\infty}^{\infty} (L-\bar{L})^2 f(L) dL \quad (2.2-2)$$

It can be easily shown that the parameter σ in Eq. (2.2-1) satisfies the definition in Eq. (2.2-2). The mean is defined in terms of the distribution function as

$$\bar{L} \equiv \int_{-\infty}^{\infty} L f(L) dL \quad (2.2-3)$$

and it can also be shown that the parameter $\bar{L}$ in Eq. (2.2-1) satisfies the definition of mean in Eq. (2.2-3).

The normal distribution is widely used in the engineering sciences, but is of little or no use in describing particle-size distributions (either population or weight basis) simply because these distributions are typically very asymmetric and are poorly represented by the normal distribution. A further objection to use of the normal distribution in describing particle-size distributions is that finite populations are predicted for negative values of the size coordinate L . However, for large ratios of $\bar{L}/\sigma$, vanishingly small populations are predicted for negative values of L and this fact in no way limits the use of this distribution function under such circumstances. The only valid objection is simply that this distribution function does not often fit the data.

The log-normal distribution function is often used in the empirical representation of particle-size distributions. This distribution function is given as

$$f(\log L) = \frac{1}{(2\pi)^{1/2}(\log \sigma')} \exp\left[-\frac{\log^2(L/\bar{L}')}{2\log^2 \sigma'}\right] \quad (2.2-4)$$

for $\log L$ in the interval $(-\infty, \infty)$ and where again σ' and $\bar{L}'$ are the two adjustable parameters of the distribution. Equation (2.2-4) is not symmetric about $\bar{L}'$ on a linear plot and, in fact, is skewed toward the larger sizes. Typically, particle distributions from comminution and precipitation processes, on a weight basis, are asymmetric and skewed toward the larger sizes, and thus the log-normal distribution is often quite useful in characterizing such particulate materials. Further, the log-normal distribution, defined for L in the interval $(0, \infty)$, overcomes the esthetic objection of predicting finite populations for negative values of L . Equation (2.2-4) is normalized over the size range L in $(0, \infty)$ such that $\int_{-\infty}^{\infty} f(\log L) d(\log L) = 1$. The parameters $\bar{L}'$ and σ' are the geometric mean and geometric standard deviation, respectively, and have definitions analogous to the normal distribution case. Thus,

$$\log \bar{L}' \equiv \int_{-\infty}^{\infty} (\log L) f(\log L) d(\log L) \quad (2.2-5)$$

and

$$\log^2 \sigma' \equiv \int_{-\infty}^{\infty} (\log L - \log \bar{L}')^2 f(\log L) d(\log L) \quad (2.2-6)$$

Again, it can be easily shown that the parameters σ' and $\bar{L}'$ of Eq. (2.2-4) satisfy definitions (2.2-6) and (2.2-5) and represent the geometric standard deviation and geometric mean, respectively.

In many cases, classification and growth processes truncate a distribution of particles below a minimum size L_1 and/or above a maximum size L_2 . A four-parameter distribution function useful for the characterization of such particle distributions is

$$f(\log L) = \frac{1}{(2\pi)^{1/2} \log \sigma'} \exp \left\{ - \left[\log \frac{(L-L_1)(L_2-L_1)}{2^{1/2} \log \sigma'} \bar{L}' \right]^2 \right\} \quad (2.2-7)$$

where L_1 , L_2 , $\bar{L}'$, and σ' are the four adjustable parameters. As $L_1 \rightarrow 0$ and $L_2 \rightarrow \infty$, Eq. (2.2-7) reduces to (2.2-4). This equation is also normalized over the particle range of interest such that

$$\int_{L=L_1}^{L=L_2} f(\log L) d\{\log[(L-L_1)/(L_2-L)]\} = 1 \quad (2.2-8)$$

The parameters $\bar{L}'$ and σ' have equivalent definitions in terms of the argument $d\{\log[(L-L_1)/(L_2-L)]\}$. Thus,

$$\log \bar{L}' \equiv \int_{L=L_1}^{L=L_2} \log [(L-L_1)(L_2-L_1)/(L_2-L)] \\ \times f(\log L) d\{\log [(L-L_1)/(L_2-L)]\} \quad (2.2-9)$$

and

$$\log^2 \sigma' \equiv \int_{L=L_1}^{L=L_2} \{\log [(L-L_1)(L_2-L_1)/(L_2-L)] - \log \bar{L}'\}^2 \\ \times f(\log L) d\{\log [(L-L_1)/(L_2-L)]\} \quad (2.2-10)$$

Again, $\bar{L}'$ and σ' as defined in Eqs. (2.2-9) and (2.2-10) are the same as the parameters in Eq. (2.2-7).

Equation (2.2-7) has been used for the representation of abnormal particle-size distributions created by classification, sieving, and/or mixing particle samples [1].

Although the log-normal distribution is purely empirical, and there is no direct relation between the parameters $\bar{L}'$ and σ' and processes governing the formation of a particle distribution, nevertheless, this distribution form is widely used in the analysis and characterization of particulate materials. Ranges of the parameters $\bar{L}'$ and σ' are often stated as part of the specifications in the purchase of granular material.

Another two parameter function useful for characterizing a one-dimensional distribution is the general gamma-type distribution function

$$f(L) = L^a \exp(-aL/b) / \Gamma(a+1)(b/a)^{a+1} \quad (2.2-11)$$

where a and b are the adjustable parameters and again $f(L)$ is normalized on the interval L in $(0, \infty)$ such that $\int_0^\infty f(L) dL = 1$. The parameter b is a measure

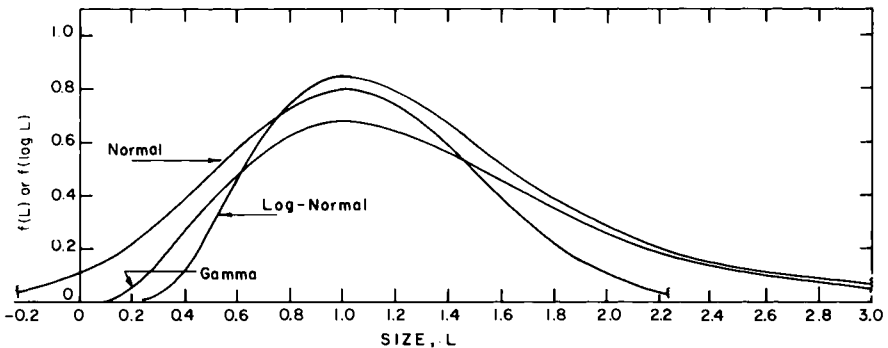


Fig. 2.2-1 Plot of three distribution functions having identical modes and coefficients of variation.

of the size of the distribution, while increasing values of the parameter a skew the distribution toward the larger sizes and narrow the distribution relative to the mean. Equation (2.2-11) is particularly useful in describing particle-size distributions from crystallization processes where the parameters a and b can be related theoretically to the process. Figure 2.2-1 plots the three distribution functions discussed thus far—normal, log-normal, and gamma—all having the same mode and relative width, on the same linear size plot.

The arithmetic mean size $\bar{L}$ and standard deviation σ do not occur as parameters in Eq. (2.2-11), but these quantities can be calculated directly from their definitions using the distribution function of Eq. (2.2-11). Thus,

$$\bar{L} = b\Gamma(a+2)/a\Gamma(a+1) = [(a+1)/a]b \quad (2.2-12)$$

and

$$\sigma = b[\Gamma(a+1)\Gamma(a+3) - \Gamma^2(a+2)]^{1/2}/a\Gamma(a) = (a+1)^{1/2}b/a \quad (2.2-13)$$

A measure of the “width” or relative size spread of a distribution is the coefficient of variation (c.v.), defined as the ratio of the standard deviation to the mean:

$$\text{c.v.} = (\sigma/\bar{L}) \times 100 \quad (2.2-14)$$

when expressed as a percentage. If σ and $\bar{L}$ are given explicitly for a distribution, the coefficient of variation can be found directly by dividing these two parameters as indicated. In general, the coefficient of variation is found by integrating over the distribution function using the definitions of $\bar{L}$ and σ . The coefficient of variation for a gamma-type distribution is

$$\text{c.v.} = 100\{[\Gamma(a+1)\Gamma(a+3)/\Gamma^2(a+2)] - 1\}^{1/2} = 100/(a+1)^{1/2} \quad (2.2-15)$$

which coefficient of variation is seen to be a function only of the parameter a and not the absolute size b .

EXAMPLE 2.2-1

The weight distribution function of crystals produced in a continuous mixed suspension crystallizer can often be represented as

$$w(x) = \frac{1}{6}x^3 \exp(-x) \quad (2.2-16)$$

where $x = L/G\tau$ is a dimensionless size, L is particle size (in centimeters), and $G\tau$ is the product of linear crystal growth rate and retention time in the

vessel (a characteristic particle size in centimeters). Find the coefficient of variation for this gamma-type distribution.

We note that this distribution is of the form

$$f(L) = L^a \exp(-aL/b) \quad (2.2-17)$$

with $a = 3$ and $b = 3G\tau$. Thus, we can use Eq. (2.2-15) to calculate the coefficient of variation: Coefficient of variation for crystal-size distribution, weight basis, is equal to $100/(a+1)^{1/2}$, or c.v. = $100/(3+1)^{1/2} = 50\%$ ♦

2.3 Properties from the Particle Distribution

In principle, a distribution function $f(L)$ completely characterizes a particle distribution and all properties of interest can be uniquely calculated, such as cumulative distributions (weight or population basis), mass or number in a finite size interval, and specific surface area.

Let $n(L)$ be a distribution function representing the distribution of population about a particle-size coordinate L for values of L in $(0, \infty)$. Further, let the distribution function represent the number of particles as a function of L per unit volume of solids-free liquid in a fluid-solid particulate system. The function $n(L)$ is then defined as the *population density* of particles in the system. By definition of the distribution function, the number of particles of size L to $L + dL$ found in a volume of liquid V (solids-free basis) is given as

$$dN = Vn(L)dL \quad (2.3-1)$$

The units of population density are thus seen to be $(\text{ft}^{-3})(\text{ft}^{-1})$, or ft^{-4} . The number of particles per unit volume of liquid in some finite size range L_1 to L_2 is found by integrating. Thus,

$$N(L_1, L_2) = \int_{L_1}^{L_2} n(L) dL \quad \text{particles in } (L_1, L_2)/\text{ft}^3 \quad (2.3-2)$$

while the total concentration of particles is given as

$$N_T = \int_0^{\infty} n(L) dL \quad \text{total particles}/\text{ft}^3 \quad (2.3-3)$$

Note that we do not require $n(L)$ to be normalized over the entire size range $(0, \infty)$, and thus this latter integral does not have the value of unity. Of course, we can define a normalized distribution function $f(L) = n(L)/N_T$ having this

property. The fraction of particles in size range L_1 to L_2 is thus

$$F(L_1, L_2) = \left[\int_{L_1}^{L_2} n(L) dL \right] / N_T \quad (2.3-4)$$

The cumulative number fraction of particles having size less than L is given as

$$F(L) = \left[\int_0^L n(p) dp \right] / N_T \quad (2.3-5)$$

The function $F(L)$ increases monotonically from 0 to 1 as L goes from 0 to ∞ .

Let the particles in the above distribution be geometrically similar. The weight of each particle can then be related to the cube of its size. Thus

$$m_p = \rho k_v L^3 \quad (2.3-6)$$

where k_v is a volumetric shape factor relating particle volume to size cubed. The shape factor is independent of size for geometrically similar particles. The mass of particles per unit volume of liquid which are in size range L to $L + dL$ is thus the mass per particle times the number of particles:

$$dM = \rho k_v L^3 n(L) dL \quad (2.3-7)$$

The mass concentration in a finite size range L_1 to L_2 is obtained by integration:

$$M(L_1, L_2) = \rho k_v \int_{L_1}^{L_2} L^3 n(L) dL \quad (2.3-8)$$

Total solids concentration in the fluid-solid system, expressed as lb/ft³ of solids-free liquid, is then given as

$$M_T = \rho k_v \int_0^{\infty} L^3 n(L) dL \quad (2.3-9)$$

The weight fraction in any size range and cumulative weight fraction distribution are then readily given as

$$W(L_1, L_2) = \rho k_v \int_{L_1}^{L_2} L^3 n(L) dL / M_T \quad (2.3-10)$$

and

$$W(L) = \rho k_v \int_0^L p^3 n(p) dp / M_T \quad (2.3-11)$$

2.3 PROPERTIES FROM THE PARTICLE DISTRIBUTION / 21

The primary distribution function can of course be a weight distribution rather than a population distribution. The weight distribution function can be obtained from differentiation of the cumulative distribution. Thus,

$$w(L) \equiv dW/dL \quad (2.3-12)$$

and the weight distribution function is thus given in terms of the population density as

$$w(L) = \rho k_v L^3 n(L)/M_T \quad (2.3-13)$$

It is obvious from Eqs. (2.3-11) and (2.3-12) that $w(L)$ is normalized over the range $(0, \infty)$ such that $\int_0^\infty w(L) dL = 1$.

A development similar to Eqs. (2.3-6)–(2.3-9) can be made for the surface area of particles in a fluid–solid system. Thus, the area of a particle is given as

$$a_p = k_a L^2 \quad (2.3-14)$$

where k_a is a shape factor relating area to size squared. The surface area per unit volume of solids-free liquid is given as

$$dA = k_a L^2 n(L) dL \quad (2.3-15)$$

while the surface area in some size range (L_1, L_2) is given as

$$A(L_1, L_2) = k_a \int_{L_1}^{L_2} L^2 n(L) dL \quad (2.3-16)$$

and the total surface area per unit volume in the suspension (ft^2/ft^3) is

$$A_T = k_a \int_0^\infty L^2 n(L) dL \quad (2.3-17)$$

EXAMPLE 2.3-1

It can be shown that for geometrically similar particles having a more or less continuous distribution of particle diameters from a minimum to a maximum, an intermediate diameter can always be chosen as the characteristic dimension L such that $k_a = 6k_v$. The volumetric shape factor k_v must of course be in reference to this characteristic size. For cubes and spheres, it is readily demonstrated that $k_a = 6k_v$. Thus, for a sphere, $v = \frac{1}{6}\pi D^3$ and $a = \pi D^2$. Choosing the characteristic dimension $L = D$ immediately gives $k_a = 6k_v$. For cubes, $v = L^3$ and $a = 6L^2$, giving directly $k_a = 6k_v$. This relationship is

true for any *equidimensioned* regular object where geometric similarity requires equal growth rates along every particle axis. This can be easily demonstrated for particles having such a constant growth rate G . Thus, equating change of volume (for a growing particle) to the rate of advance of the particle's surface gives

$$dv_p/dt = \frac{1}{2}Ga_p$$

but $v_p = k_v L^3$ and $a_p = k_a L^2$; thus,

$$3k_v L^2 dL/dt = \frac{1}{2}Gk_a L^2$$

but $dL/dt = G$; canceling GL^2 terms gives $k_a = 6k_v$.

For particles having a separate growth rate G_j , for each crystal face a_j , the above relationship is only true for the characteristic size L chosen as some suitable intermediate size. Repeating the previous derivation for this case gives

$$dv_p/dt = \sum_j (\frac{1}{2}G_j a_j)$$

Let the growth rate along the j th axis be related to the growth rate G along the characteristic axis L_c by a constant factor $G_j = c_j G = (L_j/L_c)G$. Thus, using the definition of shape factor gives

$$(d/dt)(k_v L_c^3) = \frac{1}{2}G \sum_j c_j a_j$$

or $6k_v L_c^2 = \sum_j c_j a_j$. But as $a_p = \sum_j a_j = k_a L_c^2$, then it is obvious that the relation $k_a = 6k_v$ can be preserved by choosing L_c such that $\sum_j c_j a_j = \sum_j a_j = a_p$. In practice, particle measurement techniques, such as screening, measure an average particle size such that $k_a \approx 6k_v$ even for highly irregular particles. ♦

Similar integral equations can be written in terms of the integrand $Ln(L)$ to determine the length functions in suspension (length of the crystals per unit volume laid end-to-end along their characteristic axes), but these functions are seldom calculated, because of lack of physical motivation, except as they are used in calculating average particle size.

Finally, the population distribution function can be used for calculating average particle size, weighted in some sense, in the particle suspension. The average particle size in the suspension, averaged on a population basis, is given as

$$\bar{L}_{1,0} = \left[\int_0^\infty Ln(L) dL \right] / N_T \quad (2.3-18)$$

The length-weighted average particle size is given as

$$\bar{L}_{2,1} = \int_0^\infty L [Ln(L)] dL / \int_0^\infty Ln(L) dL \quad (2.3-19)$$

The area-weighted mean particle size is given as

$$\bar{L}_{3,2} = \int_0^\infty L [L^2 n(L)] dL / \int_0^\infty L^2 n(L) dL \quad (2.3-20)$$

It is obvious that a family of possible average particle sizes is generated by the ratio of the $(i+1)$ th to the i th moment of the distribution about $L=0$. Thus, if the i th moment is defined as $m_i \equiv \int_0^\infty L^i n(L) dL$, then a suitable average particle size is given as the ratio of any two succeeding moments. Thus,

$$\bar{L}_{i+1,i} = m_{i+1}/m_i \quad (2.3-21)$$

EXAMPLE 2.3-2

Show that the parameter $\bar{L}$ in the normal distribution is the average $\bar{L}_{1,0}$. By definition of the normal distribution function, the average must be taken over all possible size ranges, namely L in $(-\infty, \infty)$. Thus,

$$\bar{L}_{1,0} \equiv \int_{-\infty}^\infty Lf(L) dL / \int_{-\infty}^\infty f(L) dL \quad (2.3-18')$$

For a normal distribution, we have Eq. (2.2-1),

$$f(L) = [1/\sigma(2\pi)^{1/2}] \exp[-(L-\bar{L})^2/2\sigma^2]$$

and

$$\int_{-\infty}^\infty f(L) dL = 1$$

Let $p = (L-\bar{L})/2^{1/2}\sigma$; then, $dL = 2^{1/2}\sigma dp$,

$$f(L) dL = \pi^{-1/2} \exp(-p^2) dp$$

Thus,

$$\bar{L}_{1,0} = \pi^{-1/2} \int_{-\infty}^\infty (2^{1/2}\sigma p + \bar{L}) \exp(-p^2) dp$$

$$\bar{L}_{1,0} = 2^{1/2}\sigma\pi^{-1/2} \int_{-\infty}^\infty p \exp(-p^2) dp + \bar{L}\pi^{-1/2} \int_{-\infty}^\infty \exp(-p^2) dp$$

The first term is an odd function integrated from $(-\infty, \infty)$ and vanishes. The second integral is equal to $\pi^{1/2}$. Thus,

$$\bar{L}_{1,0} = 0 + (\bar{L}\pi^{1/2}/\pi^{1/2})$$

or

$$\bar{L}_{1,0} = \bar{L} \quad \text{Q.E.D.} \quad \blacklozenge$$

Another closely related set of average particle sizes can be defined in terms of the population density distribution function. These are respectively the length-, area-, and mass-averaged sizes. The total length, area, and mass of a suspension, all on a unit volume basis, are defined in terms of the first, second, and third powers of these average sizes. Thus, the total particle length is given as

$$L_T = N_T \bar{L}_L \quad (2.3-22)$$

or

$$\bar{L}_L = \int_0^\infty L n(L) dL / \int_0^\infty n(L) dL = m_1/m_0 = \bar{L}_{1,0} \quad (2.3-23)$$

which is the population-weighted average size as defined in Eq. (2.3-18). Total suspension area (ft^2/ft^3) is given in terms of the area-averaged size as

$$A_T = k_a (\bar{L}_a)^2 N_T \quad (2.3-24)$$

or

$$\bar{L}_{2,0} = \bar{L}_a = \left[\int_0^\infty L^2 n(L) dL / \int_0^\infty n(L) dL \right]^{1/2} = (m_2/m_0)^{1/2} \quad (2.3-25)$$

Finally, the total mass concentration (lb/ft^3) is given in terms of the mass-averaged size as

$$M_T = \rho k_v (\bar{L}_m)^3 N_T \quad (2.3-26)$$

or

$$\bar{L}_{3,0} = \bar{L}_m = \left[\int_0^\infty L^3 n(L) dL / \int_0^\infty n(L) dL \right]^{1/3} = (m_3/m_0)^{1/3} \quad (2.3-27)$$

It is obvious from the preceding discussions that a desirable property of an empirical distribution function is that it can be easily integrated so that cumulative properties can be evaluated and so that averages can be determined in terms of moments of the distribution. These moments will then simply be functions of the parameters of the distribution. All of the averages discussed previously can be represented by the generalized equation

$$\bar{L}_{j,k} = (m_j/m_k)^{1/(j-k)}$$

EXAMPLE 2.3-3

Find the cumulative number fraction distribution of particles less than size L for a population distribution represented by a normal distribution with mean size $\bar{L}$ and standard deviation σ . Estimate the fraction of particles which this empirical form of distribution predicts to be less than size zero, assuming $\sigma/\bar{L} = 2^{-1/2}$. Thus, given

$$n(L) = c_1 \exp[-(L - \bar{L})^2/2\sigma^2] \quad (2.3-28)$$

where c_1 is some constant, the cumulative number fraction distribution is given by Eq. (2.3-5) as

$$F(L) = \left[\int_{-\infty}^L n(p) dp \right] / N_T$$

where the integration is now taken over the entire range of the distribution function, namely L in $(-\infty, L)$, and p is a dummy of integration:

$$N_T = c_1 \int_{-\infty}^{\infty} \exp[-(p - \bar{L})^2/2\sigma^2] dp \quad (2.3-29)$$

Let $z = (p - \bar{L})/2^{1/2}\sigma$; then,

$$N_T = c_1 2^{1/2}\sigma \int_{-\infty}^{\infty} \exp(-z^2) dz \quad (2.3-30)$$

This latter integral is equal to $\pi^{1/2}$. Thus,

$$N_T = c_1 \sigma (2\pi)^{1/2} \quad (2.3-31)$$

and the cumulative number distribution is then given as

$$F(L) = [1/\sigma (2\pi)^{1/2}] \int_{-\infty}^L \exp[-(p - \bar{L})^2/2\sigma^2] dp \quad (2.3-32)$$

Again making the substitution $z = (p - \bar{L})/2^{1/2}\sigma$ gives

$$F(z) = \pi^{-1/2} \int_{-\infty}^z \exp(-z^2) dz \quad (2.3-33)$$

The function $F(z)$, the cumulative normal distribution curve, cannot be integrated analytically but is widely tabulated. A solution to this integral can

be found as shown below. Breaking the integration up into two parts gives

$$\pi^{1/2}F(z) = \int_{-\infty}^0 \exp(-z^2) dz + \int_0^z \exp(-z^2) dz \quad (2.3-34)$$

Recognizing that the integrand is an even function of z , then one obtains

$$\int_{-\infty}^0 \exp(-z^2) dz = \frac{1}{2} \int_{-\infty}^{\infty} \exp(-z^2) dz = \frac{1}{2}\pi^{1/2} \quad (2.3-35)$$

Thus,

$$F(z) = \frac{1}{2} + \pi^{-1/2} \int_0^z \exp(-z^2) dz \quad (2.3-36)$$

$$F(z) = \frac{1}{2} + \frac{1}{2} \operatorname{erf}(z) \quad (2.3-36')$$

The latter function, the error function, is widely tabulated, but can be easily evaluated as follows. Let $\exp(-z^2)$ be expressed as a power series:

$$\exp(-z^2) = 1 - z^2 + \frac{z^4}{2!} - \frac{z^6}{3!} + \frac{z^8}{4!} - + \dots \quad (2.3-37)$$

Substituting this expression into Eq. (2.3-36) and integrating gives

$$F(z) = 0.5 + \frac{1}{\pi^{1/2}} \left[z - \frac{z^3}{3} + \frac{z^5}{5 \cdot 2!} - \frac{z^7}{7 \cdot 3!} + \frac{z^9}{9 \cdot 4!} - + \dots \right] \quad (2.3-38)$$

and where $z = (L - \bar{L})/2^{1/2}\sigma$. Putting $L = \bar{L}$, then $z = 0$ and $F(\bar{L}) = 0.5$, and thus we can see that the cumulative distribution function is symmetric about the mean, with half of the population being above it and half below it. Thus, the mean is also the median of the distribution.

Finally, we can use this series to estimate the number fraction which is predicted to exist for negative values of L , for the case where $\sigma/\bar{L} = 2^{-1/2}$. At $L = 0$, $z = -L/2^{1/2}\sigma = -1$,

$$\begin{aligned} F(L=0) &= 0.5 + \frac{1}{\pi^{1/2}} \left[-1.0 + \frac{1}{3} - \frac{1}{10} + \frac{1}{42} - \frac{1}{216} + \dots \right] \\ &= 0.078 \end{aligned}$$

or roughly 8% of the particle population is predicted to have negative values of particle size. ♦

EXAMPLE 2.3-4

Calculate the j th moments of the normal and log-normal distribution functions in terms of the parameters σ , $\bar{L}$ and σ' , $\bar{L}'$.

For the normal distribution, the j th moment is defined as

$$m_j \equiv [1/\sigma(2\pi)^{1/2}] \int_{-\infty}^{\infty} L^j \exp[-(L-\bar{L})^2/2\sigma^2] dL \quad (2.3-39)$$

Again define $z = (L-\bar{L})/2^{1/2}\sigma$. Thus,

$$m_j = \pi^{-1/2} \int_{-\infty}^{\infty} L^j \exp(-z^2) dz \quad (2.3-40)$$

But

$$L^j = (2^{1/2}\sigma z + \bar{L})^j \quad (2.3-41)$$

which can be expanded using the binomial expansion as

$$L^j = \sum_{r=0}^j c_r^j (2^{1/2}\sigma z)^{j-r} (\bar{L})^r \quad (2.3-42)$$

where

$$c_r^j = j!/(j-r)!r! \quad (2.3-43)$$

Substituting in Eq. (2.3-40) gives

$$m_j = \frac{1}{\pi^{1/2}} \int_{-\infty}^{\infty} \sum_{r=0}^j \left[\frac{j!}{(j-r)!r!} \right] (2^{1/2}\sigma z)^{j-r} (\bar{L})^r \exp(-z^2) dz \quad (2.3-44)$$

Recognizing that odd terms in z will integrate to zero over the interval $(-\infty, \infty)$ and interchanging integration and summation gives

$$m_j = \sum_r \frac{(2^{1/2}\sigma)^{j-r} (\bar{L})^r j!}{(j-r)!r!} \frac{1}{\pi^{1/2}} \int_{-\infty}^{\infty} z^{j-r} \exp(-z^2) dz \quad (2.3-45)$$

where

$$r = 0, 2, 4, \dots, j \quad \text{for } j \text{ even}$$

$$r = 1, 3, 5, \dots, j \quad \text{for } j \text{ odd}$$

However, the expression under the integral can be integrated to

$$\int_{-\infty}^{\infty} z^{2n} \exp(-z^2) dz = [1 \cdot 3 \cdot 5 \cdots (2n-1)/2^n] \pi^{1/2}, \quad n = 0, 1, 2, \dots \quad (2.3-46)$$

Thus, the j th moment of the normal distribution function is given as

$$m_j = \sum_r [(2^{1/2}\sigma)^{j-r} (\bar{L})^r j! \cdot 1 \cdot 3 \cdots (j-r-1)/(j-r)! 2^{(j-r)/2}] \quad (2.3-47)$$

where again

$$r = 0, 2, 4, \dots, j \quad \text{for } j \text{ even}$$

$$r = 1, 3, 5, \dots, j \quad \text{for } j \text{ odd}$$

Writing this expression out for the first few moments, in terms of the mean and coefficient of variation, $\bar{L}$ and $\sigma/\bar{L}$, the following equations result:

$$\begin{aligned} m_0 &= 1, & m_1/\bar{L} &= 1 \\ m_2/(\bar{L})^2 &= 1 + [\sigma/\bar{L}]^2, & m_3/(\bar{L})^3 &= 1 + 3[\sigma/\bar{L}]^2 \\ m_4/(\bar{L})^4 &= 1 + 6[\sigma/\bar{L}]^2 + 3[\sigma/\bar{L}]^4 \end{aligned} \quad (2.3-48)$$

Note that for a single-size distribution, $\sigma/\bar{L} = 0$, the j th moment is equal to the j th power of the (uniform) size.

For the log-normal distribution, the j th moment is defined as

$$m_j \equiv \frac{1}{(2\pi)^{1/2} \log \sigma'} \int_{-\infty}^{\infty} L^j \exp \left[-\frac{(\log L - \log \bar{L}')^2}{2 \log^2 \sigma'} \right] d(\log L) \quad (2.3-49)$$

letting $z = (\log L - \log \bar{L}')/2^{1/2} \log \sigma'$ gives

$$m_j = (\bar{L}')^j \pi^{-1/2} \int_{-\infty}^{\infty} (L/\bar{L}')^j \exp(-z^2) dz \quad (2.3-50)$$

But

$$L/\bar{L}' = \exp(2^{1/2} \log \sigma' z) \quad (2.3-51)$$

Thus,

$$m_j = (\bar{L}')^j \pi^{-1/2} \int_{-\infty}^{\infty} \exp \{ -[(-j2^{1/2} \log \sigma' z) + z^2] \} dz \quad (2.3-52)$$

Completing the square gives

$$m_j = (\bar{L}')^j \pi^{-1/2} \exp(\frac{1}{2} j^2 \log^2 \sigma') \int_{-\infty}^{\infty} \exp(-p^2) dp \quad (2.3-53)$$

where

$$p = z - j(2^{1/2}/2) \log \sigma' \quad (2.3-54)$$

Finally, recognizing the value of the above integral as $\pi^{1/2}$ gives

$$m_j = (\bar{L}')^j \exp(\frac{1}{2} j^2 \log^2 \sigma') \quad (2.3-55)$$

Or, equivalently in terms of log functions

$$\log m_j = j \log \bar{L}' + \frac{1}{2} j^2 \log^2 \sigma' \quad (2.3-56)$$

Writing this out for the first few moments gives

$$\begin{aligned} \log m_0 &= 0 & \text{or} & & m_0 &= 1 \\ \log m_1 &= \log \bar{L}' + \frac{1}{2} \log^2 \sigma' & \text{or} & & m_1/\bar{L}' &= \exp(\frac{1}{2} \log^2 \sigma') \\ \log m_2 &= 2 \log \bar{L}' + 2 \log^2 \sigma' & \text{or} & & m_2/(\bar{L}')^2 &= \exp(2 \log^2 \sigma') \\ \log m_3 &= 3 \log \bar{L}' + 4.5 \log^2 \sigma' & \text{or} & & m_3/(\bar{L}')^3 &= \exp(4.5 \log^2 \sigma') \end{aligned} \quad (2.3-57)$$

Again, for a single-size distribution,

$$\log \sigma' = 0 \quad (2.3-58)$$

and the j th moment is equal to the j th power of the size. ♦

EXAMPLE 2.3-5

Compute the j th moments of the normalized gamma distribution given by Eq. (2.2-11). By definition,

$$m_j \equiv \left(\int_0^\infty L^j L^a e^{-aL/b} dL \right) / \Gamma(a+1)(b/a)^{a+1} \quad (2.3-59)$$

Canceling $(b/a)^{a+1}$ terms and recognizing the integral as a gamma function gives

$$m_j = b^j \Gamma(j+a+1)/a^j \Gamma(a+1) \quad (2.3-60)$$

from which it is apparent that $m_0 = 1$, a necessary check on the normalization of the original distribution function. The first few moments can be written out in terms of the two parameters a and b as

$$\begin{aligned} m_1/b &= \Gamma(a+2)/a\Gamma(a+1) = (a+1)/a \\ m_2/b^2 &= \Gamma(a+3)/a^2 \Gamma(a+1) = (a+2)(a+1)/a^2 \\ m_3/b^3 &= \Gamma(a+4)/(a^3 \Gamma(a+1)) = (a+3)(a+2)(a+1)/a^3 \end{aligned} \quad (2.3-61)$$

Note that the parameter b in the distribution function is an equivalent size, and in fact is the mode of the distribution. Differentiating the gamma distribution, Eq. (2.2-11), with respect to L and setting the derivative to zero

indicates that the mode of the distribution occurs at $L = b$, independent of the parameter a . As the parameter a increases, the distribution narrows and the parameter b , the distribution mode, approaches the single uniform mean size. Thus, for $a \rightarrow \infty$, $[\Gamma(a+j+1)/a^j \Gamma(a+1)] \rightarrow 1$, and the j th moment equals the mode size raised to the j th power. ♦

EXAMPLE 2.3-6

Obtain the coefficient of variation $\sigma/\bar{L}$ in terms of moments of the distribution. Evaluate this equation for the three distributions considered thus far.

We have

$$\begin{aligned}\sigma^2 &\equiv \int_0^\infty (L - \bar{L})^2 f(L) dL \\ &= \int_0^\infty L^2 f(L) dL - 2\bar{L} \int_0^\infty L f(L) dL + \bar{L}^2 \int_0^\infty f(L) dL\end{aligned}\quad (2.3-62)$$

$$\bar{L} \equiv \int_0^\infty L f(L) dL \quad (2.3-63)$$

Thus,

$$\sigma = (m_2 - 2m_1^2 + m_1^2)^{1/2} \quad (2.3-64)$$

$$\text{c.v.} \equiv \sigma/\bar{L} = (m_2 - m_1^2)^{1/2}/m_1 \quad (2.3-65)$$

$$\text{c.v.} = [(m_2/m_1^2) - 1]^{1/2} \quad (2.3-66)$$

A. Normal Distribution

$$\text{c.v.} = \left(\frac{\bar{L}^2 + \sigma^2}{\bar{L}^2} - 1 \right)^{1/2} = \frac{\sigma}{\bar{L}} \quad (2.3-67)$$

by definition.

B. Log Normal Distribution

$$\text{c.v.} = \left\{ \frac{(\bar{L}')^2 \exp(2 \log^2 \sigma')}{[\bar{L}' \exp(\frac{1}{2} \log^2 \sigma')]^2} - 1 \right\}^{1/2} \quad (2.3-68)$$

$$\text{c.v.} = [\exp(2 \log^2 \sigma' - \log^2 \sigma') - 1]^{1/2} \quad (2.3-69)$$

$$\text{c.v.} = [\exp(\log^2 \sigma') - 1]^{1/2} \quad (2.3-70)$$

C. Gamma Distribution

$$\text{c.v.} = [(m_2/m_2^1) - 1]^{1/2} \quad (2.3-71)$$

$$\text{c.v.} = \{[\Gamma(a+3)\Gamma(a+1)/\Gamma^2(a+2)] - 1\}^{1/2} \quad (2.3-72)$$

Using the recursion relationship

$$\Gamma(a+1) = a\Gamma(a) \quad (2.3-73)$$

then

$$\text{c.v.} = \{[(a+2)/(a+1)] - 1\}^{1/2} \quad (2.3-74)$$

or finally,

$$\text{c.v.} = 1/(a+1)^{1/2} \quad \blacklozenge \quad (2.3-75)$$

Calculation of the j th moments and the cumulative distribution, as illustrated in the preceding four examples, enables one to calculate all of the pertinent properties of a particle distribution, such as total specific population, length, area, and mass, cumulative distributions of these quantities, and average size, averaged in some sense. All of these total and average quantities can be simply stated in terms of the parameters of the distribution function. A listing of such total, average, and cumulative properties for the three distributions discussed thus far, the normal, log-normal, and gamma distributions, is given in Table 2.3-1.

A distribution function, however unique in describing a particle distribution, cannot be measured directly, but must be constructed from associated measurements of the distribution. Normally, members of a population are sampled at a finite number of discrete values of the independent "size" coordinate. For example, in the case of particle-size distribution of a granular product, a deck of N screens, each of a given screen opening, is used to partition the sample into $N-1$ finite size ranges. These data can then be presented in essentially two different ways: (a) the cumulative fraction of material, on a number or mass basis, which is above or below a given size L , plotted versus the value $\bar{L}$; or (b) the fraction of material in a size increment ΔL plotted versus the average size of the increment. Plots of the former kind are cumulative size distribution plots and each point is an *exact* point on the cumulative distribution curve of the particle sample. The latter plot is a distribution plot, and, if the fractions of material are divided by their respective size increments ΔL , each data point *approximates* the distribution curve of the particle sample. The distribution curve of the particle sample represents the derivative of total material (number or weight basis) along the size axis and, as such, can only be approximately measured by direct experiment due to limitations on minimum and maximum size of the sample increment ΔL , as discussed in Section 2.1.

TABLE 2.3-1

Total, Average, and Cumulative Quantities Obtained from Some Distribution Functions of Interest

Quantity of interest ^a	Distribution form		
	Normal	Log-normal	Gamma
Distribution function (normalized)	$f(L) = \frac{1}{\sigma(2\pi)^{1/2}} \exp\left[-\frac{(L-\bar{L})^2}{2\sigma^2}\right]$	$f(\log L) = \frac{1}{(2\pi)^{1/2} \log \sigma'} \exp\left[-\frac{\log^2(L/\bar{L}')}{2 \log^2 \sigma'}\right]$	$f(L) = \frac{L^a \exp(-aL/b)}{\Gamma(a+1)(b/a)^{a+1}}$
Cumulative fraction distribution	$F(z) = 0.5 + \frac{1}{\pi^{1/2}} \times \left[z - \frac{z^3}{3} + \frac{z^5}{5 \cdot 2!} - \frac{z^7}{7 \cdot 3!} + \dots \right]$ $F(z) = 0.5 + 0.5 \operatorname{erf}(z)$ $z = (L - \bar{L})/2^{1/2}\sigma$	$F(z) = 0.5 + \frac{1}{\pi^{1/2}} \times \left[z - \frac{z^3}{3} + \frac{z^5}{5 \cdot 2!} - \frac{z^7}{7 \cdot 3!} + \dots \right]$ $F(z) = 0.5 + 0.5 \operatorname{erf}(z)$ $z = [\log(L/\bar{L}')]/2^{1/2} \log \sigma'$	$F(p) = \frac{1}{\Gamma(a+1)} \times \left[\frac{p^{a+1}}{a+1} - \frac{p^{a+2}}{a+2} + \frac{p^{a+3}}{(a+3)2!} + \dots \right]$ $p = aL/b$
jth moment	$m_j = \sum_r \frac{(2^{1/2}\sigma)^{j-r} (\bar{L})^j j! \cdot 1 \cdot 3 \cdots (j-r-1)}{(j-r)! r! 2^{(j-r)/2}}$ $j-r \text{ even}$	$m_j = (\bar{L}')^j \exp(\frac{1}{2} j^2 \log^2 \sigma')$	$m_j = \frac{b^j \Gamma(a+j+1)}{a^j \Gamma(a+1)}$
Width parameter	$\sigma = (L_{0.841} - L_{0.159})/2$	$\sigma' = L_{0.841}/L_{0.5}$	a
Size parameter	$\bar{L} = L_{0.50}$	$\bar{L}' = L_{0.50}$	$b = \text{size mode}$
Population-weighted mean size	$\bar{L}_{1,0} = \bar{L}$	$\bar{L}_{1,0} = \bar{L}' \exp(\frac{1}{2} \log^2 \sigma')$	$\bar{L}_{1,0} = [(a+1)/a]b$

Length-weighted mean size	$L_{2,1} = \bar{L} + (\sigma^2/\bar{L})$	$\bar{L}_{2,1} = \bar{L}' \exp(\frac{1}{2} \log^2 \sigma')$	$L_{2,1} = b(a+2)/a$
Area-weighted mean size	$\bar{L}_{3,2} = [(\bar{L})^3 + 3\sigma^2\bar{L}]/[(\bar{L})^2 + \sigma^2]$	$\bar{L}_{3,2} = \bar{L}' \exp(\frac{1}{2} \log^2 \sigma')$	$\bar{L}_{3,2} = b(a+3)/a$
Mass-weighted mean size	$\bar{L}_{4,3} = \frac{(\bar{L})^4 + 6\sigma^2(\bar{L})^2 + 3\sigma^4}{(\bar{L})^3 + 3\sigma^2\bar{L}}$	$L_{4,3} = \bar{L}' \exp(\frac{1}{2} \log^2 \sigma')$	$\bar{L}_{4,3} = b(a+4)/a$
Area-averaged size, $L_a = (m_2/m_0)^{1/2}$	$\bar{L}_a = [(\bar{L})^2 + \sigma^2]^{1/2}$	$\bar{L}_a = \bar{L}' \exp(\log^2 \sigma')$	$\bar{L}_a = (b/a)[(a+2)(a+1)]^{1/2}$
Mass-averaged size, $L_m = (m_3/m_0)^{1/3}$	$\bar{L}_m = [(\bar{L})^3 + 3\sigma^2\bar{L}]^{1/3}$	$\bar{L}_m = \bar{L}' \exp(\frac{1}{3} \log^2 \sigma')$	$\bar{L}_m = (b/a)[(a+3)(a+2)(a+1)]^{1/3}$
Coefficient of variation, c.v. $\equiv \sigma/\bar{L}$	c.v. $= \sigma/\bar{L} = (L_{0.841} - L_{0.159})/2L_{0.50}$	c.v. $= [\exp(\log^2 \sigma') - 1]^{1/2}$	c.v. $= \{[(a+2)/(a+1)] - 1\}^{1/2}$ $= 1/(a+1)^{1/2}$
Skewness, $\gamma_1 = \mu_3/\sigma^3$	$\gamma_1 = 0$	$\gamma_1 = \frac{\exp(4.5 \log^2 \sigma') - 3 \exp(2.5 \log^2 \sigma') + 2 \exp(1.5 \log^2 \sigma')}{[\exp(2 \log^2 \sigma') - \exp(\log^2 \sigma')]^{3/2}}$	$\gamma_1 = \frac{2}{(a+1)^{1/2}} = 2 \text{ c.v.}$
Kurtosis, $\gamma_2 = (\mu_4/\mu_2^2) - 3$	$\gamma_2 = 0$	$\gamma_2 = \frac{\exp(8 \log^2 \sigma') - 4 \exp(5 \log^2 \sigma') + 6 \exp(3 \log^2 \sigma') - 3 \exp(2 \log^2 \sigma')}{\exp(4 \log^2 \sigma') - 2 \exp(3 \log^2 \sigma') + \exp(2 \log^2 \sigma')} - 3$	$\gamma_2 = \frac{6}{a+1}$

* All mean sizes presented assume basic distribution function is a population distribution.

For these reasons, the fit of an experimental distribution to an empirical form, both qualitatively to establish the type of distribution function and quantitatively to determine the value of the parameters, is often done using cumulative size distribution data.

Consider the problem of determining the parameters $\bar{L}$ and σ for an experimental distribution which previous experience indicates can be represented by a normal distribution. A smoothed, cumulative particle-size distribution plot has been made and it is desired to find the parameters from these cumulative data. In Example 2.3-2, it was demonstrated that the mean size $\bar{L}$ was also the median. Thus, $\bar{L}$ is found directly from the cumulative curve as the size which corresponds to 0.50 on the cumulative plot. Thus,

$$\bar{L} = L[F(\bar{L})] = L_{0.5} \quad (2.3-76)$$

It is also desirable to determine σ in terms of the sizes associated with specified values of the cumulative distribution. Consider the fraction of particles in the size range $\bar{L}-\sigma$ to $\bar{L}+\sigma$, i.e., the particles within one standard deviation of the mean. Recalling the dimensionless size coordinate in Example 2.3-2, $z = (L - \bar{L})/2^{1/2}\sigma$, then the dimensionless sizes associated with the above size range are given as

$$\begin{aligned} z_- &= [(\bar{L}-\sigma) - \bar{L}]/2^{1/2}\sigma = -1/2^{1/2} \\ z_+ &= [(\bar{L}+\sigma) - \bar{L}]/2^{1/2}\sigma = 1/2^{1/2} \end{aligned} \quad (2.3-77)$$

From Eq. (2.3-38), the cumulative fraction is given as

$$F(z_-) = 0.5[1 + \text{erf}(z)] \Big|_{z=-0.707}$$

or

$$F(z_-) = 0.159 \quad (2.3-78)$$

Similarly,

$$F(z_+) = 0.841 \quad (2.3-79)$$

and it is seen that 15.9% of the distribution lies below and above the size range $\bar{L} \pm \sigma$. It then follows that σ can be determined directly from the cumulative distribution curve as

$$\sigma = \{L[F(\bar{L}+\sigma)] - L[F(\bar{L}-\sigma)]\}/2 \quad (2.3-80)$$

or

$$\text{c.v.} \equiv \sigma/\bar{L} = (L_{0.841} - L_{0.159})/2L_{0.50} \quad (2.3-81)$$

This relationship is only true for a normal distribution, but has erroneously been used in the literature as the definition of coefficient of variation for

experimental distributions bearing no necessary relationship to a normal distribution. This ratio is useful as a measure of the width of a distribution and has the advantage that it is directly and simply calculated from a cumulative plot without fitting the distribution to any given form.

The above procedure for evaluating the two parameters $\bar{L}$ and σ says nothing about whether or not the normal distribution function indeed well-represents the experimental distribution. The validity of representation of the particle distribution with a normal distribution function can be established by plotting the cumulative data on probability paper, the ordinate of which is scaled in terms of the cumulative distribution function, with the abscissa a linear scale representing particle size. The parameters σ and $\bar{L}$ can be read directly from such a cumulative plot on probability paper.

The log-normal distribution is a distribution function which forms a normal distribution in terms of the logarithm of particle size, $\log L$. Thus, the cumulative distribution function is given as

$$F(\log L) = \frac{1}{(2\pi)^{1/2} \log \sigma'} \int_{-\infty}^{\log L} \exp \left\{ -\frac{[\log(L/\bar{L})]^2}{2 \log^2 \sigma'} \right\} d(\log L) \quad (2.3-82)$$

Letting

$$p = (\log L - \log \bar{L}) / 2^{1/2} \log \sigma' \quad (2.3-83)$$

this integral becomes

$$F(p) = \pi^{1/2} \int_{-\infty}^p \exp(-p^2) dp \quad (2.3-84)$$

which has a series solution identical to the normal distribution given by

$$F(p) = 0.5 + \frac{1}{\pi^{1/2}} \left(p - \frac{p^3}{3} + \frac{p^5}{5 \cdot 2!} - \frac{p^7}{7 \cdot 3!} + \frac{p^9}{9 \cdot 4!} - + \dots \right) \quad (2.3-85)$$

$$F(p) = 0.5 + 0.5 \operatorname{erf}(p) \quad (2.3-85')$$

Again we inquire as to the fraction of particles having sizes above and below the range $\bar{L}'/\sigma'$ to $\sigma'\bar{L}$. Evaluating the variable p at these size ranges gives

$$p_- = \frac{\log(L/\bar{L}')}{2^{1/2} \log \sigma'} = \frac{\log(1/\sigma')}{2^{1/2} \log \sigma'} = -\frac{1}{2^{1/2}} \quad (2.3-86)$$

when $L = \bar{L}'/\sigma'$, and

$$p_+ = \frac{\log(L/\bar{L}')}{2^{1/2} \log \sigma'} = \frac{\log \sigma'}{2^{1/2} \log \sigma'} = \frac{1}{2^{1/2}} \quad (2.3-87)$$

when $L = \bar{L}'\sigma'$. From the series expansion of the cumulative distribution function, we obtain

$$F(p_-) = 0.159 \quad (2.3-88)$$

$$F(p_+) = 0.841 \quad (2.3-89)$$

At the size $L = \bar{L}'$, $p = \log(\bar{L}'/\bar{L}') = 0$, and from Eq. (2.3-85), it is apparent that $F(0) = 0.5$.

Thus, in a manner similar to the normal distribution case, we can obtain the parameters for the log-normal distribution from a cumulative data plot as

$$\bar{L}' = L[F(\bar{L}')] = L_{0.50} \quad (2.3-90)$$

Similarly,

$$\sigma' = \bar{L}'\sigma'/\bar{L}' = L[F(\bar{L}'\sigma')]/L[F(\bar{L}')] = L_{0.841}/L_{0.50} \quad (2.3-91)$$

Or, alternatively,

$$\sigma' = \bar{L}'/(\bar{L}'/\sigma') = L[F(\bar{L}')]/L[F(\bar{L}'/\sigma')] = L_{0.50}/L_{0.159} \quad (2.3-91')$$

And analogously to Eq. (2.3-81) for a normal distribution,

$$(\log \sigma')/(\log \bar{L}') = (\log L_{0.841} - \log L_{0.159})/2 \log L_{0.50} \quad (2.3-92)$$

Again, nothing is implied as to the degree of fit of the log-normal form of distribution by the above parameter evaluation. Cumulative distributions can be plotted on log-normal paper which utilizes a probability ordinate with log abscissa, both to verify the log-normal form of the distribution and to obtain the parameters σ' and $\bar{L}'$. Log-normal data will plot as a straight line on such coordinates.

The cumulative distribution for the normalized gamma distribution is given as

$$F(L) = \left[\int_0^L L^a \exp(-aL/b) dL \right] / \Gamma(a+1)(b/a)^{a+1} \quad (2.3-93)$$

Utilizing the transformation $x = aL/b$, then the cumulative gamma distribution is given as

$$F(a, x) = \left[\int_0^x p^a \exp(-p) dp \right] / \Gamma(a+1) \quad (2.3-94)$$

or

$$F(a, x) = P(a+1, x) \quad (2.3-95)$$

where the function $P(a+1, x)$ is the incomplete gamma function, and is widely tabulated. The function $F(a, p)$ contains the parameter a , which is unknown until the experimental data are fit to Eq. (2.3-95). Thus, a cut-and-try method is indicated for obtaining the parameters a and b . The gamma distribution is thus not as useful for the empirical representation of data as the log-normal distribution, due to the difficulty of determining the parameters a and b . However, its chief usefulness is in describing area and mass distributions for exponential population distributions where the parameter a is known.

EXAMPLE 2.3-7

Find the parameters for the normal, log-normal, and gamma distributions each having a mode of 1.0 and a coefficient of variation of 0.5. Graph these distributions on a common plot to illustrate the basic shapes of these three distributions.

A. Normal Distribution

For a normal distribution, the mean, median, and mode are identical. Thus, $\bar{L} = 1.0$:

$$\text{c.v.} = \sigma/\bar{L} = 0.5 \quad \text{or} \quad \sigma = 0.5$$

Thus, the normal distribution is given as

$$f(z) = 0.798 \exp(-z^2)$$

where $z = 1.414(L - 1)$.

B. Log-Normal Distribution

For a log-normal distribution, the mode and median are equal to the parameter $\bar{L}'$, but are not equal to the mean. Thus, $\bar{L}' = 1.0$:

$$\text{c.v.} = [\exp(\log^2 \sigma') - 1]^{1/2}$$

or $\exp(\log^2 \sigma') = 1.25$, $\log^2 \sigma' = 0.223$, $\log \sigma' = 0.472$, $\sigma' = 1.604$. Thus, the distribution function is given as

$$f(z) = 0.845 \exp(-z^2)$$

where $z = 1.5 \log L$.

C. Gamma Distribution

We have previously indicated that the parameter b is equal to the mode of a gamma distribution. Thus, $b = 1.0$; and

$$\text{c.v.} = 1/(a+1)^{1/2} = 0.5$$

or $a = 3$. Thus, the distribution function is given as

$$f(L) = 13.5L^3 \exp(-3L)$$

These three distributions, all having the same mode and coefficient of variation, are plotted for comparison in Fig. 2.2-1. Note that the log-normal distribution is normalized over the argument $\log L$, not L , and thus the area under the curve of the log-normal distribution in Fig. 2.2-1 is not unity. ♦

Thus far, two measures have been developed to describe the absolute size and the relative size uniformity of the members of a distribution. These measures are the mean $\bar{L}$ and the relative size spread or coefficient of variation $\sigma/\bar{L}$. In addition to these measures, two other numbers are often used to qualitatively indicate the shape of a distribution. These latter measures are the skewness and kurtosis of the distribution, both measured relative to a normal distribution. Skewness is a measure of the symmetry about the mean and is zero for symmetric distributions. Define the j th moment about the mean as

$$\mu_j \equiv \int_{-\infty}^{\infty} (L - \bar{L})^j f(L) dL \quad (2.3-96)$$

By definition, $\mu_1 = 0$. Recall that $\mu_j = 0$ for j odd, if $f(L)$ is an even function of $L - \bar{L}$. The skewness is defined in terms of the lowest nonvanishing odd moment μ_3 , which will be nonzero if $f(L)$ is not symmetric about $L = \bar{L}$. Thus, we define skewness in a normalized form as

$$\text{Skewness} = \gamma_1 \equiv \mu_3/\sigma^3 \quad (2.3-97)$$

In terms of the m_j moments about $L = 0$,

$$\gamma_1 = (m_3 - 3m_1 m_2 + 2m_1^3)/(m_2 - m_1^2)^{3/2} \quad (2.3-98)$$

For a normal distribution, $m_3 = \bar{L}^3 + 3\sigma^2 \bar{L}$, $m_2 = \bar{L}^2 + \sigma^2$, and $m_1 = \bar{L}$. Thus, for a normal distribution,

$$\gamma_1 = [(\bar{L}^3 + 3\sigma^2 \bar{L}) - 3\bar{L}(\bar{L}^2 + \sigma^2) + 2\bar{L}^3]/\sigma^3 = 0 \quad (2.3-99)$$

Qualitatively, $\gamma_1 > 0$ indicates a distribution skewed to the right and $\gamma_1 < 0$ indicates a distribution skewed to the left of the mean. Characteristically, particle-size distributions have positive skewness, as do the log-normal and gamma distributions.

Kurtosis is a measure of the shape of a distribution curve at the extreme ends, relative to a normal distribution. A distribution with positive kurtosis will

have a sharper peak but broader tails than a normal distribution. Kurtosis is defined for a distribution as

$$\text{Kurtosis} = \gamma_2 \equiv (\mu_4/\mu_2^2) - 3 \quad (2.3-100)$$

or, in terms of the moments about zero,

$$\gamma_2 = [(m_4 - 4m_1 m_3 + 6m_1^2 m_2 - 3m_1^4)/(m_2^2 - 2m_1^2 m_2 + m_1)] - 3 \quad (2.3-101)$$

Recognizing that for a normal distribution, $m_4 = \bar{L}^4 + 6\sigma^2 \bar{L}^2 + 3\sigma^4$, it can easily be shown that $\gamma_2 = 0$ for a normal distribution.

The four measures, $\bar{L}$, c.v., γ_1 , and γ_2 qualitatively indicate the character of a given distribution and are especially useful in describing the qualitative character of abnormal distributions. These four parameters are uniquely defined by specifying a distribution function $f(L)$. The converse is not true, and these four measures are not sufficient information to uniquely specify the distribution function $f(L)$.

2.4 Summary

In this chapter, we have indicated that more information is needed to completely specify dispersed-phase particulate systems than is needed to describe one-phase homogeneous systems. This additional information consists of a multidimensional distribution function for the particulate entities distributed about the least number of independent coordinate axes necessary to describe the state of the particles. Such independent coordinates comprise the particle phase space over which the particles are distributed. It is convenient to think of this phase space to be composed of two subregions consisting of external and internal coordinates. External coordinates give the spatial distribution of the particles, while internal coordinates refer to properties attached to each particle, e.g., size, concentration (chemical), activity, or age.

Often, a single internal coordinate is sufficient to specify a particle distribution, for example, particle-size distribution in a granular material. Such experimental distributions can often be represented empirically by analytical distribution functions. We present three distribution functions which are used for such purposes; the normal, log-normal, and gamma distributions. The normal distribution is widely used in the engineering and life sciences, especially for theoretical studies, but the latter two distributions are of more utility in characterizing particle-size distributions, mainly because of the typical skewness of such experimental distributions, which can be accounted for with the log-normal and gamma forms.

We develop the cumulative, specific and/or total, and average properties of a dispersed-phase particle distribution. These properties can be calculated directly from a population density distribution function. Cumulative functions and moments about zero are presented in terms of the two distribution parameters for the normal, log-normal, and gamma distributions. Total and average properties are expressed in terms of the leading moments of these three distribution functions as well as in terms of the two parameters of each distribution function.

Finally, we develop four quantitative measures of the qualitative nature of a distribution curve. These four measures, the mean, coefficient of variation, skewness, and kurtosis, are given in terms of both the leading moments and the two parameters for each of the three chosen distribution functions.

Nomenclature

a	Width parameter in gamma distribution	$N(L)$	Cumulative members of a population distribution
a_j	Area of j th crystal face	w	Derivative of cumulative $W(L)$ distribution
a_p	Total surface area of an individual particle of size L	$W(L)$	Cumulative weight fraction distribution
$A(L)$	Specific surface area of particles up to size L	x	Dimensionless crystal size equal to particle size divided by product of growth rate and residence time
b	Size parameter in gamma distribution, equal to mode	GREEK SYMBOLS	
$f(L)$	Normalized one-dimensional distribution function		
$F(L)$	Cumulative fraction of a distribution up to size L	ρ	Particle density
G	Linear particle growth rate	σ	Width parameter in normal distribution, equal to standard deviation
k_a	Area shape factor	σ'	Width parameter in log-normal distribution, equal to geometric standard deviation
k_v	Volumetric shape factor	τ	Mean retention time
L	Dimension in distribution function	SUBSCRIPTS	
$\bar{L}$	Arithmetic mean size in normal distribution		
L'	Geometric mean size in log-normal distribution	T	Total specific quantity in particle suspension
m_p	Total mass of individual particle		
$M(L)$	Specific mass of particles up to size L		
$n(L)$	Population density distribution function		

Reference

1. R. R. Irani and C. F. Callis, "Particle Size: Measurement, Interpretation, and Application." Wiley, New York, 1963.

THE POPULATION BALANCE

3.1 Introduction

Chapter 2 discussed the concept of multidimensional particle population distributions in particle phase space. Certain one-dimensional distribution functions were discussed. These distribution functions are useful in the *empirical* characterization of particle distributions. An obvious limitation of such empirical characterization is the difficulty of relating the parameters in the distribution function to the factors in the process environment which produced the given distribution. In this chapter, we shall develop a *predictive* multidimensional particle distribution theory which, in the case of certain well-defined regular processes of particle formation, is useful in the *a priori* prediction of the *form* and often the *magnitude* of the particle distribution. The distribution function is defined by the solution of a differential equation, rather than given by a specific algebraic form. The physical parameters affecting the formation of the distribution are nested in the differential equation, thus allowing the theory to be useful in a predictive as well as a descriptive sense. In addition, the transient response of particle processes can be quantitatively described by this theory.

3.2 Particle Phase Space

Particle phase space consists of the least number of independent coordinates attached to a particle distribution which allow a complete description of the

properties of the distribution. Particle phase space may conveniently (and arbitrarily) be divided into two subregions given by internal and external particle coordinates. External coordinates refer simply to the spatial distribution of the particles. Such external coordinates are of course unnecessary, for example, in the description of a well-mixed particulate process, although it may be quite convenient to report the distribution on a unit-volume basis. Internal coordinate properties refer to those properties attached to each individual particle and which quantitatively measure its state, independent of its position. The prime example of an internal coordinate property is particle size; other examples would be chemical activity (e.g., of a catalyst particle), particle age (since birth or since entering a particular environment), chemical composition (as for a particle or droplet undergoing mass transfer), and particle energy content.

In the following treatment, we will consider an $(m+3)$ -dimensional particle distribution function $n(R, t)$ defined over a region R consisting of the three spatial dimensions plus m independent internal property coordinates. From the definitions in Chapter 2, the number of particles existing at time t in an incremental region of particle phase space dR is given as

$$dN = n dR \quad (3.2-1)$$

while the total number of particles in some finite subregion of particle phase space R_1 is

$$N(R_1) = \int_{R_1} n dR \quad (3.2-2)$$

We shall presently make use of these definitions in formulating a population balance of particles in the particle phase space.

3.3 Population Fluxes: Convection, Birth, and Death

In any particulate process giving rise to the formation of a particle distribution, individual particles are continually changing their position in the particle phase space, i.e., each particle moves along the various internal and external coordinate axes. If these changes are gradual and continuous, we refer to this movement as a convection along the respective particle coordinates and refer to the rate of change of the coordinate property of a particle as the convective particle velocity along that coordinate axis. Thus, we define the vector particle phase-space velocity as

$$\mathbf{v} = v_x \delta_x + v_y \delta_y + v_z \delta_z + v_1 \delta_1 + v_2 \delta_2 + \cdots v_m \delta_m$$

or

$$\mathbf{v} = \mathbf{v}_e + \mathbf{v}_i \quad (3.3-1)$$

where the v 's are the particle velocity components and the δ 's are the unit vectors along the external and internal coordinate axes. It should be noted that the external velocity $\mathbf{v}_e$ is not necessarily the same as the fluid velocity $\mathbf{u}$ in a particle suspension. In general, particle velocity must be computed from the fluid velocity $\mathbf{u}$ and a suitable momentum exchange (friction factor) relationship in an auxiliary force balance for each particle. In a well-mixed suspension, motions $\mathbf{u}$ and $\mathbf{v}_e$ are both quite random and no attempt would be made to follow particle motion in the external particle phase-space coordinates.

The internal particle velocities $\mathbf{v}_i$ are assumed to be a unique function of the state of the particle. An example of internal convective velocity is that of the linear rate of growth of a crystal in a supersaturated solution, determined by the size of the particle and the level of surrounding supersaturation. As discussed in Chapter 1, the definition of the linear size of a particle is often a difficult choice and certainly depends on how particle size is measured. However, given the definition of particle size L , the linear growth rate is just the rate of change of L . Thus, $G = dL/dt$, where G is the convective velocity of a particle along the L axis. An important restriction that will be made in developing this particle-size distribution theory is that *each* particle behaves identically at a given point in particle phase space. Thus, for the case of linear growth rate, G may vary with particle size and/or position in the suspension, but each particle of the same size and in the same environment (i.e., at the same state in phase space) would grow at the same linear growth rate.¹

Finally, we recognize the possibility of particles suddenly appearing or disappearing at a point in the internal particle phase space, which can be represented by birth and death functions of the particle distribution. Again, we restrict our attention to regular processes where these birth and death events can be related (at least statistically) to the state of the total system and/or to the position of a particle in the particle phase space. An example of birth and

¹ In the case of crystal growth, evidence indicates that crystals of identical size and environment do not necessarily grow at the same rate, but there is an inherent dispersion of particle growth rates under identical conditions. If a given particle has a repeatable growth rate under identical conditions, then it behaves properly in its particle phase space and one can view the growth dispersion phenomenon as the result of having a distribution of particle phase planes in the suspension with each particle being a member of one of the phase planes. Alternatively, one can say that the distribution was not adequately represented by a single coordinate axis, particle size, but should be represented by a two-dimensional distribution, say particle size plus inherent growth activity. The latter internal property is perhaps given by dislocation density on the crystal surface, which would be an exceedingly difficult property to relate to the state of the crystal. Thus, an inherently two-dimensional distribution might reasonably be described, in an engineering sense, using one-dimensional distribution theory, with the result that the unaccounted-for growth dispersion phenomenon would produce a "smearing" of the distribution not predicted by the one-dimensional theory. Fortunately, in the case of crystallization, residence-time distribution factors override growth dispersion effects in determining the particle-size distribution.

death events is particle breakage in a suspension. Breakage of a given particle results in a death event at the original particle size and birth events at the sizes of the resulting pieces. Such death events might reasonably be statistically correlated with the position of the particle in particle phase space (say particle size), while birth events at a given particle size would depend on the entire distribution of particles (state of the total system) above that size. Such a description might involve integrals of the distribution function, with the result that the particle distribution would be described by solution of a set of integro-differential equations.

Let B and D represent such empirical birth and death functions at a point in phase space. The net appearance of particles at a given point is then given as $(B - D) dR$. It should be emphasized that this formulation is only symbolic and is of little value unless reasonable theoretical or empirical forms for these birth and death terms can be stated in terms of the distribution function and point in particle phase space as discussed above.

3.4 Particle-Number Continuity Equation

A population balance for particles in some fixed subregion of particle phase space can be stated as

$$\text{Accumulation} = \text{Input} - \text{Output} + \text{Net generation} \quad (3.4-1)$$

If we consider the subregion, say R_1 , to move convectively with the particle phase-space velocity $\mathbf{v}$, i.e., take the Lagrangian viewpoint, then the population balance for particles in subregion R_1 may be stated simply as

$$\frac{d}{dt} \int_{R_1} n dR = \int_{R_1} (B - D) dR \quad (3.4-2)$$

The former term may be expanded, using Leibnitz's rule, to

$$\frac{d}{dt} \int_{R_1} n dR = \int_{R_1} \frac{\partial n}{\partial t} dR + \left(n \frac{d\mathbf{x}}{dt} \right) \Big|_{R_1} = \int_{R_1} \left[\frac{\partial n}{\partial t} + \nabla \cdot \left(\frac{d\mathbf{x}}{dt} n \right) \right] dR \quad (3.4-3)$$

where $\mathbf{x}$ is the set of internal and external coordinates comprising the phase space R . Recognizing that

$$d\mathbf{x}/dt = \mathbf{v} = \mathbf{v}_e + \mathbf{v}_i \quad (3.4-4)$$

the population balance can be written for the Lagrangian region R_1 as

$$\int_{R_1} [\partial n / \partial t + \nabla \cdot (\mathbf{v}_e n) + \nabla \cdot (\mathbf{v}_i n) + D - B] dR = 0 \quad (3.4-5)$$

As the region R_1 was arbitrary, the integrand must vanish identically. Thus, the population balance is given as

$$\partial n / \partial t + \nabla \cdot (\mathbf{v} n) - B + D = 0 \quad (3.4-6)$$

or, in terms of the $m+3$ coordinates,

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x}(v_x n) + \frac{\partial}{\partial y}(v_y n) + \frac{\partial}{\partial z}(v_z n) + \sum_{j=1}^m \frac{\partial}{\partial x_j} [(v_i)_j n] - B + D = 0 \quad (3.4-6')$$

Equation (3.4-6) is a number continuity equation in particle phase space. This equation, together with mass and energy balances, which constrain the values of the internal coordinate velocities $\mathbf{v}_i$, particle-number formation kinetics² (nucleation kinetics), and side conditions representing entry or exit of particle suspension from the region of interest, completely determine the formation and dynamics of multidimensional particle distributions formed in processes obeying the very general restraints discussed in this chapter. Equation (3.4-6) is completely general and is used when the particles are distributed along both external and internal coordinate space. More convenient, but more restricted forms of the population balance will subsequently be developed.

EXAMPLE 3.4-1

Reduce Eq. (3.4-6') to obtain the differential equation governing the formation of the particle-size distribution of crystals produced in an isothermal plugflow crystallizer with negligible breakage operating at steady state. Indicate a method of solution from the form of the population balance equation, and outline the auxiliary equations needed for complete solution of the problem.

² Note that $B(L)$ is *not* the nucleation rate, as nuclei are assumed to be of zero size. However, the birth function $B(L)$ could represent the nucleation rate if nuclei were spontaneously formed as a distribution over a finite size range. For convenience, the nucleation rate can be introduced by the birth function by allowing

$$B = \begin{cases} B^0, & L = 0 \\ 0, & L > 0 \end{cases}$$

At steady state, with negligible breakage, the population balance reduces to

$$\nabla \cdot \mathbf{v}_e n + \sum_{j=1}^m \frac{\partial}{(\partial x_i)_j} [(v_i)_j n] = 0 \quad (3.4-7)$$

The external coordinate system may be represented by the single crystallizer length dimension x , while the internal coordinate may be taken as particle size L . Thus, the population balance becomes

$$\frac{\partial}{\partial x}(v_x n) = -\frac{\partial}{\partial L}(Gn) \quad (3.4-8)$$

where $G \equiv \partial L / \partial t$ is the linear crystal growth rate. For small particles and high velocities, the particle velocity v_x may be taken as the plugflow velocity u_x . Assuming that growth rate remains independent of size, an empirical observation known as McCabe's ΔL law which often holds true, then Eq. (3.4-8) reduces to

$$\partial n / \partial x = -(G/u_x) \partial n / \partial L \quad (3.4-9)$$

This equation is similar to the one-dimensional wave equation and thus suggests the method of characteristics for solution. Defining the characteristic s in the x - L plane by the differential equation

$$\partial L / \partial x = G/u_x, \quad (3.4-10)$$

and the derivative operator along the characteristic as

$$\frac{d}{ds} \equiv \frac{\partial}{\partial x} + \frac{G}{u_x} \frac{\partial}{\partial L} \quad (3.4-11)$$

it is apparent that along the characteristic curve in the x - L plane,

$$dn/ds = 0 \quad (3.4-12)$$

Thus, population density is constant along a characteristic. Calculation of characteristic curves in the x - L plane thus allows the calculation of the particle-size distribution at any point x in the crystallizer.

Side conditions and auxiliary equations necessary for solution of the population balance are:
growth rate

$$G = G(C) \quad (3.4-13)$$

density of nuclei

$$n(0, x) = B^0(C)/G(C) \quad (3.4-14)$$

and a mass balance

$$u_x dC/dx = -\frac{1}{2}\rho k_a G \int_0^\infty n(L, x) L^2 dL \quad (3.4-15)$$

with boundary conditions

$$C(0) = C^0, \quad n(L, 0) = f(L) \quad \blacklozenge \quad (3.4-16)$$

Solution of the above set of integrodifferential equations would, in principle, uniquely define the particle-size distribution at each point in the isothermal plugflow crystallizer. Note that in the above equations, the two dependent variables C and n are respectively one- and two-dimensional distributions. This incompatibility of dimension results in the difficult-to-solve integro-partial-differential form of the equations. A transformation to eliminate this difficulty will be presented in a subsequent section.

3.5 Population Balance over a Macroscopic External Coordinate Region

In practice, many engineering problems involving dispersed-phase particulate systems are carried out in one or more regions which can each be considered to be well-mixed. In such cases, the chief concern is not the spatial distribution of particles, but rather, the system can be described knowing only the distribution of particles in the internal phase space. Equation (3.4-6), which is distributed in both external and internal phase space, can be transformed by averaging in the external phase space to yield a much more useful equation for such backmixed systems. Thus, we choose a suitable volume $V(t)$ of external phase space having an arbitrary number of inputs and outputs of flow rate Q_k and population density n_k and integrate the population balance over this region. We need consider only one region, as any complex multistage recycle process can always be decomposed into separate regions with only input and output streams. Multiplying Eq. (3.4-6) by dV and integrating over $V(t)$ gives

$$\int_V (\partial n / \partial t + \nabla \cdot \mathbf{v}_e n + \nabla \cdot \mathbf{v}_i n + D - B) dV = 0 \quad (3.5-1)$$

As the suspension is mixed, n , D , and B are functions only of time and the internal coordinates and can be taken out of the integration. The second term, an integral over the volume of the spatial divergence of the population flux, can be converted into a surface integral of the population flux flowing through

the moving surfaces of the system. Thus,

$$\int_V \nabla \cdot \mathbf{v}_e n dV = \int_{S_m} v_N n dS \quad (3.5-2)$$

where v_N is the average particle velocity normal to the surface and S_m is the sum of all moving surfaces of the system. S_m may be considered to be composed of three components:

a. The k input and output streams to the volume V . The integral of $v_N n dS_m$ over these streams represents the inflow and outflow of slurry to the system. These terms can be represented as

$$\int_{S_k} v_N n dS = \sum_k Q_k n_k \quad (3.5-3)$$

where Q_k is taken as positive for flow out of V and negative for flow into V (sign convention assuming outward-directed normal to surface is positive).

b. Changes in system volume due to accumulation at a free interface. The contribution of this term, assuming n is independent of position, is

$$\int_{S_s} v_N n dS = n \int_{S_s} v dS = n dV_s/dt \quad (3.5-4)$$

where V_s is the change at the free surface of the solids-free volume of liquid in the system and S_s is the free surface of liquid in the vessel.

c. Change in void fraction of solids in the system. The contribution of this term for a mixed suspension is

$$n \int_{S_e} v_N dS = -n dV_e/dt \quad (3.5-5)$$

where V_e is the volume of the system occupied by the solids and S_e is the total particle-fluid interface.

The total rate of change of solids-free volume³ is due to changes at a free

³ Population density can be based either on solids-free or total volume. In the latter case, the term dV_e/dt would vanish and the only change in volume would be due to changes in total system volume at a free interface. In any case, the term dV_e/dt is negligible for "thin" suspensions. Basing the population density on solids-free liquid basis avoids problems such as making nucleation rate a function of void fraction, at the price of having void volume appear in the population balance. The two viewpoints, n based on solids-free or total volume, are completely equivalent.

surface and to changes of void fraction. Thus,

$$dV/dt = (dV_s/dt) - (dV_e/dt) \quad (3.5-6)$$

and the total contribution of the last two terms can be written as

$$\int_{S_e} v_N n dS + \int_{S_s} v_N n dS = n dV/dt \quad (3.5-7)$$

Thus, the total contribution of the spatial population flux divergence term is given as

$$\int_V \nabla \cdot \mathbf{v}_e n dV = \sum_k Q_k n_k + n dV/dt \quad (3.5-8)$$

and the spatial-averaged population balance may be written as

$$V(\partial n/\partial t + \nabla \cdot \mathbf{v}_i n + D - B) + n dV/dt = - \sum_k Q_k n_k \quad (3.5-9)$$

Or, dividing by V and rearranging,

$$\partial n/\partial t + \nabla \cdot \mathbf{v}_i n + n d(\log V)/dt = B - D - \sum_k (Q_k n_k/V) \quad (3.5-10)$$

Equation (3.5-10), the macroscopic population balance, is averaged in external phase space and distributed in internal phase space. It is the most useful form of the population balance and is used for describing transient and steady-state particle-size distributions in well-mixed vessels.

EXAMPLE 3.5-1

Simplify the macroscopic population balance to describe the transient particle-size distribution in a continuous, constant-volume, isothermal, well-mixed crystallizer with mixed product removal. Assume the crystallizer feed streams are free of suspended solids and that the crystallizer operates with negligible breakage. Writing the macroscopic population balance, Eq. (3.5-10) gives

$$\frac{\partial n}{\partial t} + \frac{\partial(Gn)}{\partial L} + D - B + n \frac{d(\log V)}{dt} = - \sum_k \frac{n_k Q_k}{V} \quad (3.5-11)$$

The breakage and volume accumulation⁴ terms can be set equal to zero as indicated above. The right-hand side of Eq. (3.5-11) represents only the mixed

⁴ Assuming a "thin" suspension with negligible change in solids-free volume.

suspension discharge. Again assuming McCabe's ΔL law, Eq. (3.5-11) reduces to

$$\frac{\partial n}{\partial t} + G \frac{\partial n}{\partial L} + \frac{n}{\tau} = 0 \quad (3.5-12)$$

where $\tau = V/Q_0$ is the drawdown time of the vessel. Additional constraints and side conditions necessary for the solution of Eq. (3.5-12) are, for initial distribution, density of nuclei, and growth rate,

$$n(0, L) = f(L) \quad (3.5-13)$$

$$n^0 = B^0(C)/G(C) \quad (3.5-14)$$

$$G = G(C) \quad (3.5-15)$$

respectively, and a dynamic mass balance on solute being crystallized,

$$\frac{dC}{dt} = \frac{Q_i C_i}{V} - \frac{Q_o C}{V} - \frac{\rho k_a G}{2} \int_0^\infty n L^2 dL \quad (3.5-16)$$

Many inorganic systems operate with negligible supersaturation, i.e., operate very near the solubility diagram even in transient operation. In such systems, the per-pass yield is essentially constant at 100%, independent of the particle-size distribution. For such high-yield systems, supersaturation is immeasurable, and may be eliminated as a parameter, with density of nuclei correlated to crystal growth rate. For such systems, side and auxiliary equations (3.5-14) and (3.5-16) can be simplified to

$$n^0 = n^0(G) \quad (3.5-17)$$

and

$$G = (1/3\tau) \int_0^\infty n L^3 dL / \int_0^\infty n L^2 dL \quad (3.5-18)$$

the latter resulting from equating the instantaneous rate of make to the instantaneous production rate. However, invariance of yield implies that solids concentration is constant and hence the third moment of the particle distribution is invariant. Thus, Eq. (3.5-18) may be written as

$$G = M_\tau / \left(3\rho k_v \tau \int_0^\infty n L^2 dL \right) \quad (3.5-19)$$

and growth rate is seen to be inversely proportional to crystal area at constant rate of make. ♦

These equations for transient particle-size distribution in a well-stirred, isothermal, mixed-product removal crystallizer have been extensively studied and the results of these studies will be discussed in detail in a subsequent chapter.

EXAMPLE 3.5-2 TRANSIENTS IN A CLOSED GRINDING CIRCUIT

Utilize the macroscopic population balance, Eq. (3.5-10), to describe transient particle-size distribution in a closed-circuit grinding mill as shown in Fig. 1.3-1. Indicate the empiricisms necessary to describe this system.

Assuming that all size reduction occurs via the birth and death functions, rather than in a continuous manner, $v_i = G = 0$, and we need not consider convection along an internal coordinate. Further, we recognize that there would be some size distribution gradients in the axial direction but the typical ball mill, being as large in diameter as in length, more nearly approaches the backmixed than the plugflow condition. Thus, Eq. (3.5-10), using the nomenclature from Fig. 1.3-1, reduces to

$$\frac{\partial n}{\partial t} = B(L, n) - D(L) + \frac{Q_F n_F}{V} + \frac{Q_R n_R}{V} - \frac{Q_T n}{V} \quad (3.5-20)$$

where the Q 's and V are solids-free water flow rates and ball mill holdup, respectively, and where the birth function $B(L, n)$ is indicated to depend on size L as well as the distribution n above L which could conceivably breakdown to size L . The death function $D(L)$ is merely the rate of breakage at a given size (number/ft³-hr- μ m), and for constant mill configuration and operation, would depend only on particle size. The birth function B must of course be consistent with D , as birth events result from death events. Specific forms for the birth and death functions are considered in Chapter 7.

To complete a description of the system, n_R must be related to n through a size-separation description of the classifier. Hydroclones operate by excluding oversize from the overflow rather than concentrating the undersize. Thus, if the fraction of feed material at a given size reporting to the underflow is plotted versus size, the separation curve, for zero size, asymptotically approaches the underflow to feed ratio Q_R/Q_T , and asymptotically approaches unity as size increases. The size at which 50% of the particles are removed from the overflow is termed the size-separation or "cut point" of the classifier under those conditions of operation. A typical classification curve for hydroclone separation is shown as Fig. 3.5-1, where it is seen that the classification function $P(L)$ can be closely represented by a straight line joining the two asymptotes Q_R/Q_T and 1.0 over one sieve size above and below the cut point, i.e., $L_c/2^{1/2}$ to $L_c 2^{1/2}$. The separation curve for a particular cyclone under a particular set

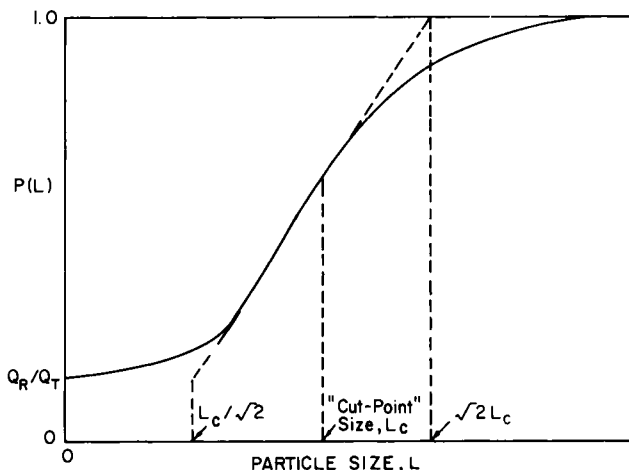


Fig. 3.5-1 Typical size-classification curve for hydroclone classifier (Preprint 71-B-78 presented at the AIME Meeting, New York, March 3, 1971).

of operating conditions can of course be determined by direct measurement of feed and underflow particle-size distributions.

Assuming the classification curve is known, the recycle stream can be related to the grind distribution and flow as

$$Q_R n_R = P(L) Q_T n \quad (3.5-21)$$

Thus, the transient particle-size distribution in a closed-circuit grinding mill can be represented as

$$\frac{dn}{dt} = B(L, n) - D(L) + \frac{Q_F n_F}{V} + \frac{P(L)-1}{V} Q_T n \quad (3.5-22)$$

where the empirical functions B , D , and P must be ascertained from the particular geometric and operating conditions of the mill. ♦

It should be emphasized that Eq. (3.5-22) represents the open-loop (i.e., uncontrolled) dynamics of the closed-circuit grinding mill described, under the restriction of constant slurry density, and that additional dynamical equations would have to be added to describe a closed-loop system wherein manipulation of flows and/or slurry density were implemented in response to changing mill conditions.

3.6 Moment Transformation of Population Balance

In many systems of engineering interest, a knowledge of the complete particle distribution is unnecessary. Rather, some average or total quantities are sufficient to represent the particle distribution. In Chapter 2, we discussed how these average or total properties, such as average size or surface area or mass concentration, could be obtained in terms of integrals of the distribution function—in particular, moments of the distribution.

Further, Example 3.4-1 alluded to a basic incompatibility of the population balance equation *vis a vis* the transport equations for mass, momentum, and energy; namely that these equations are respectively of $m + 3$ and 3 dimensions. This difference in dimensionality leads to difficulty in simultaneous solution of the transport equations together with the population balance equation, usually resulting in integrodifferential equations as illustrated in Examples 3.4-1 and 3.5-1.

Thus, we seek a transformation of the population balance equation which will average the distribution with regard to the internal coordinate properties and which will reduce the dimensionality to that of the transport equations. This closed set, with appropriate side conditions, can be thought of as a complete mathematical representation of particulate systems, a general theory of particulate systems holding under the stated restrictions.

Assume a spatially distributed particulate process which can be described adequately with one internal coordinate⁵ in particle phase space. The population balance can be written for this system as

$$\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{v}_e n + \frac{\partial}{\partial L}(Gn) = B - D \quad (3.6-1)$$

where the single internal coordinate L can be thought of as particle size. Assume that the particle growth rate $G = dL/dt$ varies no more than linearly with particle size. Thus,

$$G = G_0(1 + aL) \quad (3.6-2)$$

Define the j th moment of the distribution as

$$m_j(\mathbf{x}_e, t) = \int_0^\infty n L^j dL \quad (3.6-3)$$

⁵ The following moment transformation can be applied to a multidimensional internal distribution, obtaining mixed moments along the internal coordinates x_1 and x_2 of the form $m_{j,k} = \int_0^\infty \int_0^\infty x_1^j x_2^k n dx_1 dx_2$. Further, these moments form a closed set under the conditions, for each axis, of Eq. (3.6-8). However, the mathematical difficulty of recovering a multivariate distribution from the set of mixed moments limits utility of the moment transformation to a single internal coordinate (see Hulburt and Katz [1]).

The population balance can now be averaged in the L dimension by multiplying by $L^j dL$ and integrating from zero to infinity. Thus,

$$\int_0^\infty L^j \left[\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{v}_e n + \frac{\partial}{\partial L} (Gn) - B + D \right] dL = 0 \quad (3.6-4)$$

Reversing order of integration and differentiation gives the first two terms as

$$\int_0^\infty L^j \left(\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{v}_e n \right) dL = \frac{\partial m_j}{\partial t} + \nabla \cdot \mathbf{v}_e m_j \quad (3.6-5)$$

which assumes that $\mathbf{v}_e \neq \mathbf{v}_e(L)$.

In general, the birth and death terms, B and D , will be given in terms of the distribution function n as well as the independent coordinates $\mathbf{x}_e$ and L . Assume that the spatial averaging (moment integration) of these functions can be expanded in terms of the first k moments of the distribution, $m_0, m_1, \dots, m_k$. Thus, we write

$$\int_0^\infty [B(\mathbf{x}_e, L, n, t) - D(\mathbf{x}_e, L, n, t)] L^j dL = \bar{B}(\mathbf{x}_e, t, m_k) - \bar{D}(\mathbf{x}_e, t, m_k) \quad (3.6-6)$$

$j = 0, 1, 2, \dots \geq k$

Finally, the third term in the population balance can be integrated by parts to give

$$\int_0^\infty L^j \frac{\partial}{\partial L} (Gn) dL = -0^j \cdot B^0 - jG_0(m_{j-1} + am_j) \quad (3.6-7)$$

where B^0 is the number flux entering the internal coordinate region at $L = 0$ (the nucleation rate in the case of crystallization). The moment transformation of the population balance for one internal coordinate can thus be written as

$$\frac{\partial m_j}{\partial t} + \nabla \cdot \mathbf{v}_e m_j = 0^j \cdot B^0 + jG_0(m_{j-1} + am_j) + \bar{B} - \bar{D}, \quad (3.6-8)$$

$j = 0, 1, 2, \dots \geq k$

For any maximum integer $j = J$, Eqs. (3.6-8) form a closed set in terms of the moments m_j . Notice that it was necessary to limit the dependency of the growth rate to the first power of L as well as the expansion of the birth and death functions to the k th-order moment ($k \leq J$) in order to close the set at the J th moment. Equations (3.6-8) are observed to be of the same dimensionality as the transport equations and can be solved side by side with the equations of mass, momentum, and energy transport to yield a complete

mathematical description of the particulate process. Further, average and/or total properties of the distribution can be obtained directly from these time- and position-dependent moments. Such information is often sufficient to describe the particulate phase. In effect, this moment transformation has resulted in a tradeoff in which the dimensionality of the system has been reduced by one at the price of obtaining average, rather than distributed, information concerning the particle-size distribution. Alternatively, one can view this transformation as a tradeoff between a single four-dimensional equation, to an infinite set of three-dimensional equations, which can fortunately be truncated to a finite set, usually three or four equations, the third moment (fourth equation) entering in the mass balance and closing the set. Computationally, this transformation is often of great utility.

Finally, the question of dynamic stability of a particulate process can be answered by solving the truncated set of moment equations. Certainly, instability of the averaged quantities (moments) indicates instability of the distributed system. This technique will be illustrated in a later chapter.

EXAMPLE 3.6-1

Write the moment equations for the isothermal, plugflow crystallizer described previously in Example 3.4-1.

Assuming steady state, negligible breakage, and a particle velocity equal to the plugflow velocity u_x , the moment equations reduce to

$$u_x \frac{dm_j}{dx} - 0^j \cdot B^0 = jGm_{j-1}, \quad j = 0, 1, 2, \dots \quad (3.6-9)$$

which again assumes $G \neq G(L)$. The question now arises, "How many moment equations should be retained in the simulation?" Assuming that the entire distribution as a function of size⁶ is not required, but rather the amount of yield to solid material and/or average properties are desired, then this question is answered by writing the equations to the highest moment interacting with side conditions and auxiliary equations. Thus, we write the mass balance and boundary conditions. The mass balance is given as

$$u_x \frac{dC}{dx} = -\frac{\rho G k_a m_2}{2} \quad (3.6-10)$$

which is seen to involve the second moment of the particle distribution.

⁶ See Section 3.8 for a discussion of the recovery of a distribution function from its first k moments.

Finally, growth rate and nucleation rate are given by their respective kinetic equations as

$$B^0 = B^0(C) \quad (3.6-11)$$

$$G = G(C) \quad (3.6-12)$$

Assuming an unseeded pregnant feed liquor, an additional set of side conditions that must be met are

$$m_j(0) = 0 \quad (3.6-13)$$

$$C(0) = C^0 \quad (3.6-14)$$

The moment equations are thus closed at the second moment and the moment equations and mass balance can be solved simultaneously to obtain yield and average properties of the distribution, all as a function of position in the reactor. ♦

3.7 Macro-Moment Equations

The moment transformation can also be applied to the spatially averaged, or macroscopic, form of the population balance. Thus, multiplying the macroscopic balance by $L^j dL$ and integrating on $(0, \infty)$ gives

$$\int_0^\infty L^j \left[\frac{\partial n}{\partial t} + \frac{\partial}{\partial L} (Gn) + n \frac{d(\log V)}{dt} + \sum_k \frac{Q_k n_k}{V} + D - B \right] dL = 0 \quad (3.7-1)$$

where again the single internal particle coordinate L can be thought of as particle size.

The first, third, and fourth terms can be integrated directly to give

$$\int_0^\infty L^j \left[\frac{\partial n}{\partial t} + n \frac{d(\log V)}{dt} + \sum_k \frac{Q_k n_k}{V} \right] dL = \frac{dm_j}{dt} + m_j \frac{d(\log V)}{dt} + \sum_k \frac{Q_k m_{j,k}}{V} \quad (3.7-2)$$

Again, assuming the growth rate varies with no more than the first power of size L , the second term can be integrated by parts to give Eq. (3.6-7),

$$\int_0^\infty L^j \frac{\partial}{\partial L} (Gn) dL = -0^j \cdot B^0 - jG_0(m_{j-1} + am_j)$$

Assuming the birth and death terms can be expanded in terms of the first k moments, these terms can be written symbolically as in Eq. (3.6-6). Thus, the macro-moment form of the population balance is given as

$$\frac{dm_j}{dt} + m_j \frac{d(\log V)}{dt} = jG_0(m_{j-1} + am_j) + 0^j \cdot B^0 - \sum_k \frac{Q_k m_{j,k}}{V} + \bar{B} - \bar{D},$$

$$j = 0, 1, 2, \dots \quad (3.7-3)$$

Note that the only derivative remaining is the ordinary derivative with respect to time. At steady state, these equations reduce to a set of nonlinear, algebraic equations.

EXAMPLE 3.7-1

Write the macro-moment equations for the transient, well-mixed isothermal crystallizer described in Example 3.5-1. Using the limiting approximation of a high-yield, constant-slurry-density crystal system, then solids-free volume is also constant in a constant-total-volume system. Thus, the term $d(\log V)/dt$ vanishes. Assuming liquid feeds and a single mixed discharge, the summation and subscript k can be dropped from the slurry input-output terms. Again, assume $G \neq G(L)$. Equation (3.7-3) can thus be written for the well-stirred, constant-yield, constant-volume, isothermal, dynamic crystallizer as

$$\frac{dm_j}{dt} + \frac{m_j}{\tau} - 0^j \cdot B^0 = jGm_{j-1}, \quad j = 0, 1, 2, \dots \quad (3.7-4)$$

Again, the question of how many moments to include in the simulation must be answered from the goals of the study. Assuming that the transient particle-size distribution is not to be recovered from the moments, the set may be closed after the second moment. This may be seen by writing the side conditions and auxiliary constraints

$$G = k/m_2 \quad (3.7-5)$$

$$B^0 = B^0(G) \quad (3.7-6)$$

with initial conditions

$$m_j(0) = m_j^0 \quad (3.7-7)$$

These auxiliary equations involve no moments higher than m_2 and the set can be closed after the second moment. These equations will be examined in a later chapter to investigate the problem of dynamical stability of particle-size distribution in a mixed suspension crystallizer. ♦

3.8 Recovery of the Particle-Size Distribution Function from the Moments

In the previous section, we transformed the population balance equation, distributed along one internal coordinate axis, into a set of J equations in terms of the first J moments of the particle distribution defined as

$$m_j(\mathbf{x}_e, t) \equiv \int_0^\infty n(\mathbf{x}_e, L, t) L^j dL, \quad j = 0, 1, 2, \dots, J \quad (3.8-1)$$

We now ask the question, "Given a set of the first J moments of a distribution function, can we reconstruct the original function in some approximate sense?" Obviously, a continuous distribution function, containing an infinite amount of information, cannot be exactly specified with the finite information contained in a finite set of numbers $\{m_j\}$. Yet, we might hope to recover n from a limited set $\{m_j\}$ to an accuracy adequate for, and an amount of effort consistent with, the aims of an engineering simulation of a particulate process. Two such techniques will be discussed here.

An elegant method of recovering an approximate distribution function from a set of J leading moments $\{m_j(\mathbf{x}_e, t)\}$ has been proposed [2]. This technique utilizes an expansion of the distribution in terms of a gamma distribution with polynomial correction terms involving Laguerre polynomials having moment-dependent coefficients. The parameters in the leading gamma distribution are matched with m_0, m_1, m_2 and thus the polynomial corrections have coefficients involving only the third and higher moments. Specifically, this inversion is given by

$$n(\mathbf{x}_e, L, t) = \frac{(\lambda/a)(\lambda L/a)^{\lambda-1} e^{-\lambda L/a}}{(\lambda-1)!} \left[m_0 + \sum_{n=3}^J k_n \ell_n^{(\lambda)} \left(\frac{\lambda L}{a} \right) \right] \quad (3.8-2)$$

where the parameters λ and a are given in terms of moments up to m_2 as

$$a = m_1/m_0, \quad \lambda = a^2/[(m_2/m_0) - a^2] \quad (3.8-3)$$

The n th-order Laguerre polynomial and n th coefficient are given respectively as

$$\ell_n^{(\lambda)}(p) = \sum_{j=0}^n (-1)^j \frac{n!(n+\lambda-1)!}{j!(n-j)!(n+\lambda-1-j)!} p^{n-j} \quad (3.8-4)$$

and

$$k_n = \sum_{j=0}^n (-1)^j \frac{(\lambda-1)!(\lambda/a)^{n-j}}{j!(n+\lambda-1-j)!(n-j)!} m_{n-j} \quad (3.8-5)$$

For gamma distributions, Eq. (3.8-2) is exact in its leading term and the two parameters in the gamma distribution need only be determined from Eqs. (3.8-3).

EXAMPLE 3.8-1

Figure 3.8-1 replots the log-normal distribution of Fig. 2.3-1 having a mode size of 1.0 and coefficient of variation of 0.5. This distribution was approximated with the gamma function-Laguerre polynomial expansion of Eqs. (3.8-2) and (3.8-3). Note that the moments for the log-normal distribution are given analytically from Eq. (2.3-55) as

$$m_j = (\bar{L}')^2 \exp(\frac{1}{2} j \log^2 \sigma')$$

and thus there should be no numerical errors in describing the distribution through the j th moment by the set $\{m_j\}$. The technique finds the “best-fit,” two-parameter normalized gamma distribution using the moments m_0, m_1, m_2 , as per Eq. (3.8-3), and then uses the higher moments to correct this first approximation using Laguerre polynomial correction terms. Figure 3.8-1 indicates that the leading term, the gamma distribution, is a good fit to the log-

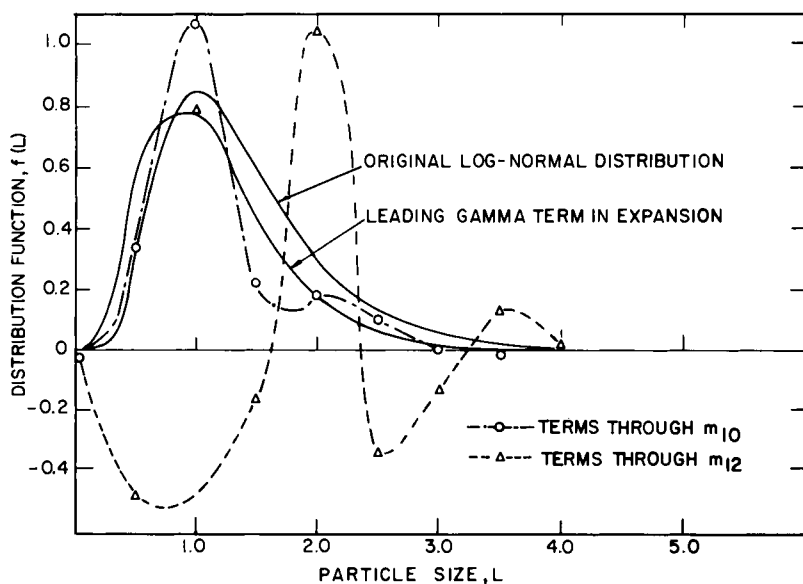


Fig. 3.8-1 Approximation of a distribution function by series expansion in terms of leading moments.

normal distribution. However, higher-order corrections involving the Laguerre polynomial terms produce oscillations about the gamma distribution. These oscillations grow with an increasing number of terms, thus making the method of no practical value. Figure 3.8-1 plots the original log-normal distribution having a mode of 1.0 and a coefficient of variation of 0.5 together with the gamma distribution having identical m_0 , m_1 , and m_2 (which of course implies equal $\bar{L}$ and c.v.). As the gamma and log-normal distributions are not unlike each other in form, this first gamma-distribution approximation is seen to be a good representation of the desired log-normal function. However, adding higher-order Laguerre polynomial terms to the approximation only worsens the degree of fit, as shown by the expansion involving the first ten moments. These oscillations grow with the number of moments retained in the expansion and the approximation is useless when the first 16 moments are included. ♦

A less elegant, but more useful, technique for the approximate recovery of the distribution function is described below.

The j th moment is written as

$$m_j = \int_0^{\infty} n L^j dL \quad (3.8-6)$$

This integral, to a first-order approximation, is given as

$$m_j = \sum_{k=1}^N n_k L_k^j \Delta L_k \quad (3.8-7)$$

where n_k is the value of n at the midpoint L_k of a size range ΔL_k . Rewriting Eq. (3.8-7) as a linear combination of the N ordinate values of the distribution $\{n_k\}$ gives

$$m_j = \sum_{k=1}^N a_k^{(j)} n_k \quad (3.8-8)$$

where

$$a_k^{(j)} = L_k^j \Delta L_k \quad (3.8-9)$$

The set of moments to $(N-1)$ th order can then be written in matrix notation as

$$\mathbf{m} = \mathbf{A} \mathbf{n} \quad (3.8-10)$$

where the matrix $\mathbf{A}$ is the $N \times N$ matrix of coefficients $a_k^{(j)}$. Thus, we write the elements of the matrix $\mathbf{A}$ as

$$a_{jk} = L_k^j \Delta L_k \quad (3.8-11)$$

Equation (3.8-10) represents a set of N linear algebraic equations in terms of N values of population density and can easily be inverted by standard techniques to obtain an approximate distribution function given at N values of L . This technique has proven quite satisfactory in practical engineering simulations.

The question of how many moments should be included in the inversion must be determined by numerical experimentation. Higher moments unduly weight the distribution toward the larger sizes, where perhaps the distribution is not well-defined and where it is possible for the continuum assumption in the particle continuity equation to fail. Preliminary calculations with Eq. (3.8-10) indicate that 8–10 moments satisfactorily reproduce an original empirical distribution.

3.9 Summary

In this chapter, we have developed the need for a *predictive* as well as a *descriptive* theory of multivariable particle distributions in particulate processes. The population balance (number-continuity) equation together with associated mass, momentum, and energy transport equations and with appropriate boundary conditions involving mass and number kinetics provide a unified predictive theory for such regular particulate systems obeying the restrictions implicit in the derivation of these equations. This population balance was presented in four forms, each having advantages in the description of certain systems. These four forms of the population balance, together with restrictions and advantages of that form, are listed below for easy reference.

A. Micro-Distributed Population Balance

From Eq. (3.4-6), we have

$$\partial n / \partial t + \nabla \cdot \mathbf{v}_e n + \nabla \cdot \mathbf{v}_i n = B - D$$

Uses and characteristics: (a) most general form of population balance; (b) emphasizes mathematical similarity with mass continuity equation; (c) useful for spatially distributed systems.

Assumptions and limitations: (a) particles are numerous enough to approximate a continuum; (b) each particle has identical trajectory in particle phase space.

B. Macro-Distributed Population Balance [Eq. (3.5-10)]

$$\partial n / \partial t + \nabla \cdot \mathbf{v}_i n + n d(\log V) / dt = - \sum_k (Q_k n_k / V) + B - D$$

Uses and characteristics: (a) useful for backmixed systems in any configuration; (b) reduces to ordinary differential equation for steady-state distribution along one internal coordinate; (c) birth and death functions may be expressed in any form that can be computed numerically.

Assumptions and limitations: (a) same as micro distributed equations; (b) suspension is mixed or balance is over all particles in suspension with average B , D , and $\mathbf{v}_i$; (c) only internal coordinate particle distributions are considered.

C. Micro-Moment Population Balance [Eq. (3.6-8)]

$$\partial m_j / \partial t + \nabla \cdot \mathbf{v}_e m_j = 0^j \cdot B^0 + jG_0(m_{j-1} + am_j) + \bar{B} - \bar{D}, \quad j = 0, 1, 2, \dots$$

Uses and Characteristics: (a) reduces dimensionality of population balance to transport equations; (b) reduces magnitude of computation for spatially distributed systems; (c) averages internal coordinate in naturally occurring moments.

Assumptions and limitations: (a) same as micro-distributed equation; (b) birth and death terms, if used, must be independent of n or expandable in terms of leading moments; (c) only one internal coordinate considered.

D. Macro-Moment Population Balance [Eq. (3.7-3)]

$$\frac{dm_j}{dt} + m_j \frac{d(\log V)}{dt} = jG_0(m_{j-1} + am_j) + 0^j \cdot B^0 - \sum_k \frac{Q_k m_{j,k}}{V} + \bar{B} - \bar{D},$$

$$j = 0, 1, 2, \dots$$

Uses and characteristics: (a) reduces dimensionality of population balance to only time dependence, i.e., ordinary differential equation; (b) useful for stability and transient studies of particle distributions; (c) averages internal coordinate in terms which occur in auxiliary equations and constraints.

Assumptions and limitations: same as micro-distributed, macro-distributed, and micro-moment equations.

The above four forms of the population balance equations, together with the transport equations and auxiliary side conditions, form a complete mathematical theory of particulate systems. The only restrictions to the use of these equations are those listed above and the individual's adeptness for using mathematical equations to represent physical reality.

Finally, this chapter presented a brief outline of techniques which can be used to recover, in some approximate sense, a particle distribution function from the first k moments of the distribution. In some cases, it appears that the

most efficient method of solution of these particle equations is to solve the moment equations together with, and with the same dimensionality of, the transport equations and then to recover the particle-size distribution from the moments.

Nomenclature

$B(L)$	Particle birth function at size L	u	Solution velocity
$\bar{B}$	Transformed birth function in moment equation	$\mathbf{v}$	Particle velocity in region R
B^0	Nucleation rate	$\mathbf{v}_e$	External (spatial) particle velocity
C	Solute concentration	$\mathbf{v}_i$	Internal particle velocity
D	Particle death function at size L	V	Suspension volume
$\bar{D}$	Transformed death function in moment equation	$\mathbf{x}$	Vector coordinates of region R
G	Linear particle growth rate	GREEK SYMBOLS	
k_a	Area shape factor		
k_v	Volumetric shape factor		
L	Particle size	ρ	Particle density
m_j	j th moment of population distribution	τ	Mean particle retention time
n	Population density at size L	SUBSCRIPTS	
n^0	Population density of nuclei		
$P(L)$	Size separation function of hydroclone classifier		
Q	Volumetric flow rate	e	Fluid-particle interface
R	Region in particle phase space	F	Feed stream
s	Particle characteristic	i	Inlet stream
S	Surface bounding particle suspension	k	k th stream
		m	Moving surface
		o	Outlet stream
		R	Recycle stream
		s	Free surface
		T	Total

References

1. H. M. Hulburt and S. Katz, *Chem. Eng. Sci.* **19**, 555 (1964).
2. H. M. Hulburt and S. Katz, *Chem. Eng. Sci.* **19**, 572-574 (1964).

THE STEADY-STATE MSMPR CRYSTALLIZER

The previous chapters have dealt with the ideas inherent in the mathematical description of the particle-size distributions in dispersed systems. It was pointed out that the preferred distribution representations are those which derive directly from the physics and chemistry of the process by which they are produced. This means that the adjustable parameters and the form should arise directly from the process. In the case of crystallization, the crystal-size distribution depends on the kinetics of nucleation and growth as well as the constraints and the geometry of the system. The influence of these factors should be evidenced in the distribution function. We will now show how the size distribution of the product of a continuous mixed-suspension, mixed-product-removal (MSMPR) crystallizer is obtained.

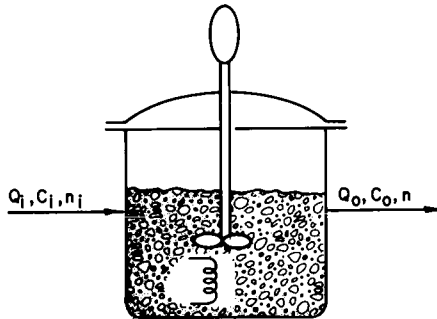


Fig. 4.1-1 Schematic representation of MSMPR crystallizer.

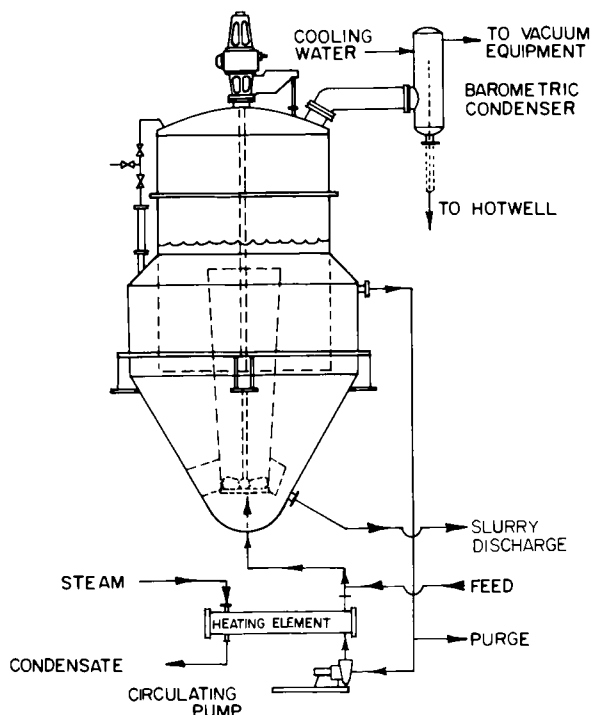


Fig. 4.1-2 Schematic diagram of industrial draft-tube baffle (DTB) crystallizer [after R. C. Bennett and M. Van Buren, *Chem. Eng. Progr. Symp. Ser.* 95 65, 44 (1969)].

4.1 Definition of System and Constraints

We now consider a continuously fed crystallizer of volume V , containing crystals dispersed in mother liquor as shown in Figure 4.1-1. In the general case, it can be assumed that seed crystals are present in the feed stream and that both growth and nucleation are taking place in the volume V because of supersaturation. The supersaturation could be generated by chemical reaction, evaporation, or cooling. The following detailed treatment is specifically for a cooling system, although the result is applicable to other types.

Crystallizers of the continuous mixed-suspension, mixed-product-removal type are widely used in industry and the laboratory. The constraints and conditions permitting this type of operation are relatively easy to attain. Figure 4.1-2 illustrates an industrial crystallizer of the draft-tube baffle (DTB) type, which normally approximates these constraints. Such crystallizers behave as though they are perfectly mixed. That is, in any arbitrarily small element of the volume, regardless of its location in the mixed section of the crystallizer,

a full and uniform particle-size continuum can be assumed to exist. Further, such a crystallizer has unclassified withdrawal. This means the particle-size distribution of the product crystals is the same as the distribution in the volume V of the crystallizer.

In many systems, crystal breakage or attrition is negligible except for fracture, which results in minute particles of near-nucleus size with no measurable reduction in the size of the parent crystal.

It is also quite common for crystals of different sizes to have the same crystal habit or shape. If this is the case, the crystal size may be represented by one characteristic linear dimension, usually the second longest axis. In practice, the size is usually the size of a standard screen through which it just passes. If the habits of different sizes are the same, the volume, mass, or area of a crystal can be determined by use of an appropriate shape factor.

The above characterizing dimension will be given the symbol L and will be the screen size of the particle. The rate at which this dimension grows will be termed the growth rate G .

In conformance with previous developments, we will represent the distribution of sizes in terms of a population density n , defined such that

$$\Delta N = \int_{L_1}^{L_2} n \, dL \quad (4.1-1)$$

where ΔN is the number of crystals in size range L_1 to L_2 per unit volume of suspension, with n being some function of L yet to be determined. The population density n has dimensions¹ of numbers/length-volume. If L_1 and L_2 represent the sizes of two adjacent screens in a stack of testing sieves, ΔN is the number of crystals on the sieve in size range L_1 to L_2 in a unit volume of suspension.

In conformity with the discussion above, the constraints and assumptions used in the subsequent analysis may be summarized as follows: (a) perfect mixing; (b) no classification at withdrawal; (c) breakage assumed negligible; (d) uniform shape factor.

Steady-state operation requires that the feed rate, composition, and temperature remain constant, and that the crystallizer volume and temperature remain constant.

4.2 The Crystal Population Balance

The number of crystals in a given size range must be conserved with no accumulation if the system described in Section 4.1 is to operate at steady state.

¹ In the following development, we choose suspension volume, rather than mother liquor volume, as the basis.

That is, the number rate of crystals entering a size range must equal the number rate leaving. We now use this requirement to derive the form of the size distribution.

Consider an arbitrary size range L_1 to L_2 in the volume V in Fig. 4.1-1, having population density n_1 and n_2 , respectively, at sizes L_1 and L_2 . The growth rate of crystals of size L_1 is G_1 and that of size L_2 is G_2 . For an increment of time Δt , the number of crystals entering this range because of growth is given by

$$V n_1 G_1 \Delta t \quad (4.2-1)$$

Similarly, the number of crystals leaving by growth is

$$V n_2 G_2 \Delta t \quad (4.2-2)$$

If the feed stream contains seed crystals in this range, then the input to the distribution in the volume V is

$$Q_i \bar{n}_i \Delta L \Delta t \quad (4.2-3)$$

where Q_i is the volumetric flow rate, $\bar{n}_i$ is the average population density in the range L_1 to L_2 in the feed, and $\Delta L = L_2 - L_1$.

Similarly, the number removal by bulk flow of crystals in this range is given by

$$Q \bar{n} \Delta L \Delta t \quad (4.2-4)$$

The output subscripts in the above term have been dropped because of the assumption of mixed removal. Combining Eqs. (4.2-1), (4.2-2), (4.2-3), and (4.2-4) in a number balance gives: Input to size range ΔL = output from size range ΔL , or

$$Q_i \bar{n}_i \Delta L \Delta t + V G_1 n_1 \Delta t = Q \bar{n} \Delta L \Delta t + V G_2 n_2 \Delta t \quad (4.2-5)$$

Dropping the Δt 's and rearranging gives

$$V(G_2 n_2 - G_1 n_1) = (Q_i \bar{n}_i - Q \bar{n}) \Delta L \quad (4.2-6)$$

Clearly, as ΔL approaches zero, the average values of n become point values and the equation takes the form

$$V d(Gn)/dL = Q_i n_i - Q n \quad (4.2-7)$$

For an unseeded system or at least for a system which has no crystals in the

input large enough to be in the size range under consideration, $n_i = 0$ and

$$(V/Q)d(Gn)/dL + n = 0 \quad (4.2-8)$$

This is the useful form for the population balance obtained from a MSMPR crystallizer. Under most industrial conditions, McCabe's ΔL law may be assumed to hold. This requires that G not be a function of L . Using this assumption and defining τ , the drawdown time, equal to V/Q gives

$$G\tau(dn/dL) + n = 0 \quad (4.2-9)$$

This result can also be obtained by writing the steady-state version of the macrobalance, Eq. (3.5-12), $(\partial n/\partial t) + G(\partial n/\partial L) + (n/\tau) = 0$, which reduces to Eq. (4.2-9), $G\tau(dn/dL) + n = 0$.

We now define n^0 as the population density of the embryo-size crystals and we let the size of these crystals be vanishingly close to zero. Using this boundary condition, Eq. (4.2-9) can be integrated,

$$\int_{n^0}^n dn/n = - \int_0^L dL/G\tau \quad (4.2-10)$$

which gives

$$n = n^0 \exp(-L/G\tau) \quad (4.2-11)$$

Equation (4.2-11) represents the expected number distribution of the crystal product obtained from a crystallizer satisfying the assumptions and constraints discussed in Section 4.1. We note that it was derived for a cooling crystallizer but that it is not restricted to systems with that particular method of producing supersaturation. Equations (4.2-9)–(4.2-11) are applicable to MSMPR crystallizers so long as the holding time τ is the mean residence time of the crystals in suspension. In the case of mixed product removal, this is true if $\tau = V/Q_o$, where V is the crystallizer volume and Q_o is the slurry withdrawal rate.

The MSMPR concept has been used widely in the laboratory as well as in practice. Figure 4.2-1 shows a typical precipitation-type laboratory crystallizer used at the University of Arizona. Industrial systems of this kind are also used. Typical of these are the draft-tube baffle (Fig. 4.1-2) and forced circulation (FC) systems used widely in evaporative crystallization. These systems are designed to circulate the magma so that the solids in suspension will be well mixed and so that solids are present at the boiling surface. The result is a more uniform level of supersaturation throughout the crystallizer, which results in lower nucleation rates. Even very large crystallizers approximate the well-mixed conditions and produce size distributions represented by Eq. (4.2-11).

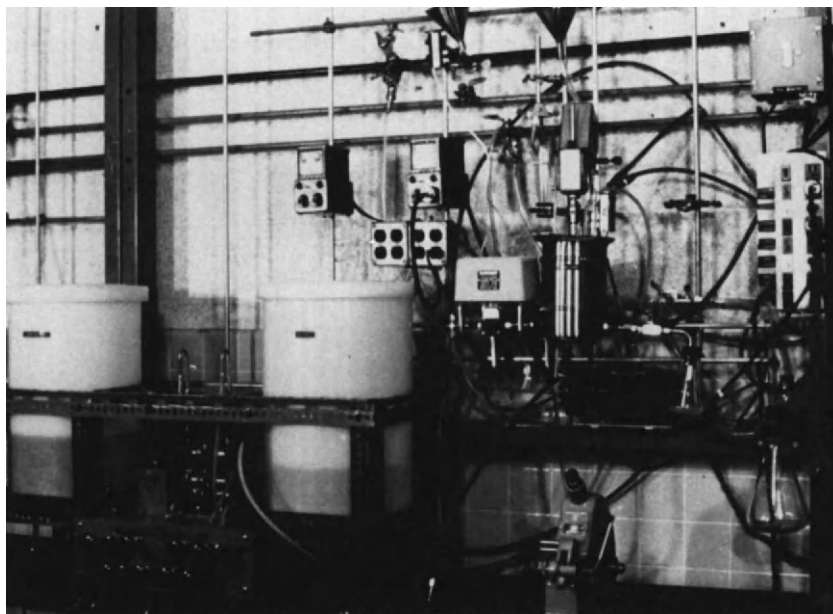


Fig. 4.2-1 Bench-scale MSMPR crystallizer used to obtain nucleation-growth kinetics. Supersaturation may be generated by cooling or by salting-out with miscible third component. (Apparatus used in the Chemical Engineering Department, University of Arizona.)

4.3 Significance of the Distribution Representation

The distribution represented by Eq. (4.2-11) has many advantages over an empirically formed distribution representation. Although it is a two-parameter model, each parameter can be related to the kinetics of the system and the imposed system constraints.

The parameter $G\tau$ is the product of the crystal growth rate and the mean residence time of the crystals in suspension. The growth rate G is directly determined by the kinetics of growth and τ is the drawdown time, which is known in any operating system. In practice, one cannot, in general, fix these two quantities independently. As we shall see later, one fixes the mass and energy flows and the kinetics of nucleation and growth peculiar to the crystal system determine the growth rate which exists. The adjustable controls include the feed concentration, rate of energy input or removal, and the feed rate.

The parameter n^0 , the population density of nucleus-size crystals, is related to the kinetics of nucleation in the following way.

Let the nucleation rate B^0 be represented by

$$B^0 = (dN/dt)|_{L \rightarrow 0} = dN^0/dt \quad (4.3-1)$$

Note that the dimensions of (4.3-1) are number/time-volume. The growth rate G may be thought of as the differential dL/dt . Thus,

$$(dN/dt)|_{L \rightarrow 0} = [(dL/dt)(dN/dL)]_{L \rightarrow 0} \quad (4.3-2)$$

Remembering that

$$dN^0/dL = (dN/dL)_{L \rightarrow 0} = n^0 \quad (4.3-3)$$

gives

$$B^0 = n^0 G \quad (4.3-4)$$

The parameter n^0 therefore “contains” the nucleation kinetics, by Eq. (4.3-4). We see then that the parameters are related to the crystallization rates operative in the system. These rates derive from the fundamental kinetic laws for nucleation and growth and the constraints imposed on the system, i.e., system parameters such as flow rate, vessel size, concentrations, and energy input or removal rate.

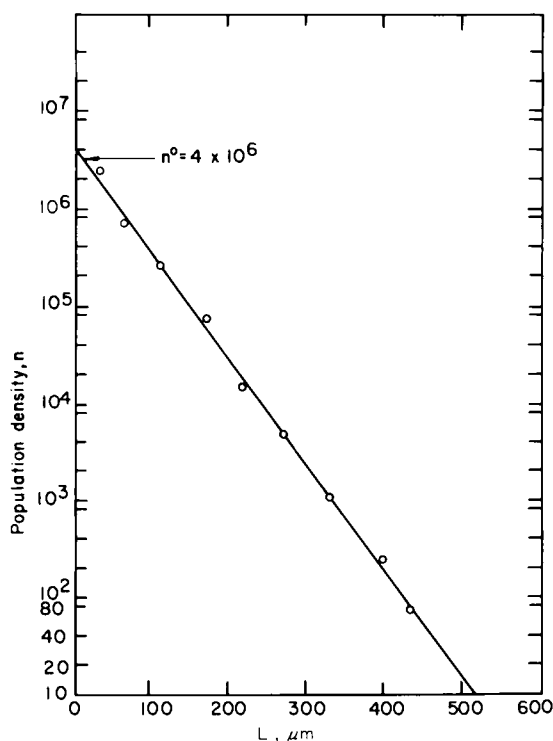


Fig. 4.3-1 Semi-log population density plot from MSMPR crystallizer.

EXAMPLE 4.3-1

Suppose that the crystal product from a system such as that described in Section 4.1 is sized and the population density function determined. If the data are plotted on semi-log paper, it should form a straight line as shown in Fig. 4.3-1. The slope of the line is $-1/2.303G\tau$. With the holding time or draw-down time equal to 15 min, the growth rate from Fig. 4.3-1 is $2.7 \mu\text{m}/\text{min}$.

The intercept n^0 is 4×10^6 number/ μm -liter. Multiplying n^0 and G gives

$$B^0 = (4 \times 10^6)(2.7) = 10.8 \times 10^6 \text{ number/liter-min}$$

the nucleation rate. ♦

This example shows how the growth and nucleation rates can be determined simultaneously and shows how these rates affect the distribution. In Chapter 9, we discuss the experimental procedure and data obtained by exploiting this relationship.

We note that the form of the distribution remains the same regardless of the fundamental kinetic laws of nucleation and growth so long as growth rate G is not a function of crystal size L . This being the case, we can generalize on the properties of this distribution by using a dimensionless form. Let $y = n/n^0$ and $x = L/G\tau$. Substituting these quantities into Eq. (4.2-11) gives

$$y = \exp(-x) \quad (4.3-5)$$

The above equation describes the dimensionless distribution function for the MSMR crystallizer. In the next section, we will show how this equation can be used to develop information about crystallizing systems.

4.4 The Exponential Distribution

For practical purposes, one is not usually interested in the number distribution, but in the mass or weight distribution. In fact, frequently, the distribution is represented only by the mass-averaged size and a coefficient of variation. We now show how these other distributions for the MSMR crystallizer can be obtained from the fundamental number distribution function n .

From the definition of the population density, the total number of crystals in a unit volume of a system was given in Section 2.3 by Eq. (2.3-3),

$$N_T = \int_0^\infty n(L) dL$$

We assume of course the function $n(L)$ is such that the integral converges. For the exponential distribution, this is the case, and therefore

$$N_T = \int_0^{\infty} n^0 \exp(-L/G\tau) dL \quad (4.4-1)$$

or

$$N_T = m_0 = n^0 G\tau \quad (4.4-2)$$

The above is termed the zeroth moment of the distribution and represents the number of crystals in the volume under consideration.

Similarly, the higher moments represent other physical quantities pertaining to the crystals in a crystallizer. The first moment is termed the specific length L_T and is the sum of the characteristic lengths of all the crystals in the distribution. The second moment multiplied by an area shape factor is the specific surface area of the distribution. The third moment multiplied by a volume shape factor represents the specific volume of the crystals in the distribution. If the third moment is also multiplied by the crystal mass density, the product is the specific mass of crystals in the distribution. These moments are summarized as

$$\begin{aligned} L_T = m_1 &= \int_0^{\infty} L n^0 \exp(-L/G\tau) dL \\ &= n^0 (G\tau)^2 \end{aligned} \quad (4.4-3)$$

$$\begin{aligned} A_T = k_a m_2 &= k_a \int_0^{\infty} L^2 n^0 \exp(-L/G\tau) dL \\ &= 2k_a n^0 (G\tau)^3 \end{aligned} \quad (4.4-4)$$

$$\begin{aligned} M_T = k_v m_3 \rho &= k_v \rho \int_0^{\infty} L^3 n^0 \exp(-L/G\tau) dL \\ &= 6\rho k_v n^0 (G\tau)^4 \end{aligned} \quad (4.4-5)$$

Equations (4.4-4) and (4.4-5) are applications of Eqs. (2.3-17) and (2.3-9). Equation (4.4-3) was included to complete the picture.

It is convenient to discuss these moments in dimensionless form and define the number, length, area, and mass cumulative fractions as F , $\mathcal{L}$, $\mathcal{A}$ and W , respectively, as previously discussed in Section 2.3. Using Eq. (4.3-5) gives

$$\begin{aligned} F = N/N_T &= \int_0^x \exp(-x) dx / \int_0^{\infty} \exp(-x) dx \\ &= 1 - \exp(-x) \end{aligned} \quad (4.4-6)$$

$$\begin{aligned}\mathcal{L} = L/L_T &= \int_0^x x \exp(-x) dx / \int_0^\infty x \exp(-x) dx \\ &= 1 - \exp(-x)(1+x)\end{aligned}\quad (4.4-7)$$

$$\begin{aligned}\mathcal{A} = A/A_T &= \int_0^x x^2 \exp(-x) dx / \int_0^\infty x^2 \exp(-x) dx \\ &= 1 - \exp(-x)(1+x+\tfrac{1}{2}x^2)\end{aligned}\quad (4.4-8)$$

$$\begin{aligned}W = M/M_T &= \int_0^x x^3 \exp(-x) dx / \int_0^\infty x^3 \exp(-x) dx \\ &= 1 - \exp(-x)(1+x+\tfrac{1}{2}x^2+\tfrac{1}{6}x^3)\end{aligned}\quad (4.4-9)$$

At the outset of this discussion, we were concerned with the number density or the distribution function representing the distribution of numbers. We now generalize and define the dimensionless distribution functions for length, area, and mass as well. Let y , ℓ , a , and w be the distribution functions for number, length, area, and mass, respectively. Differentiating Eqs. (4.4-6)–(4.4-9) gives

$$y(x) - \frac{d}{dx}[1 - \exp(-x)] = \exp(-x) \quad (4.4-10)$$

$$\ell(x) = \frac{d}{dx}[1 - \exp(-x)(1+x)] = x \exp(-x) \quad (4.4-11)$$

$$a(x) = \frac{d}{dx}\left[1 - \exp(-x)\left(1+x+\frac{x^2}{2}\right)\right] = \frac{x^2 \exp(-x)}{2} \quad (4.4-12)$$

$$w(x) = \frac{d}{dx}\left[1 - \exp(-x)\left(1+x+\frac{x^2}{2}+\frac{x^3}{6}\right)\right] = \frac{x^3 \exp(-x)}{6} \quad (4.4-13)$$

These functions are plotted in Fig. 4.4-1. The function $w(x)$ is the distribution function used in Example 2.2-1 to calculate the coefficient of variation. Similar coefficients of variation can be determined for functions (4.4-11) and (4.4-12).

Two parameters are required to specify the above distribution of the MSMPR crystallizer. In addition to the coefficient of variation, a convenient second parameter is the average size. A number of averages were defined as in Section 2.3 by Eqs. (2.3-18)–(2.3-20). For the exponential distribution, these

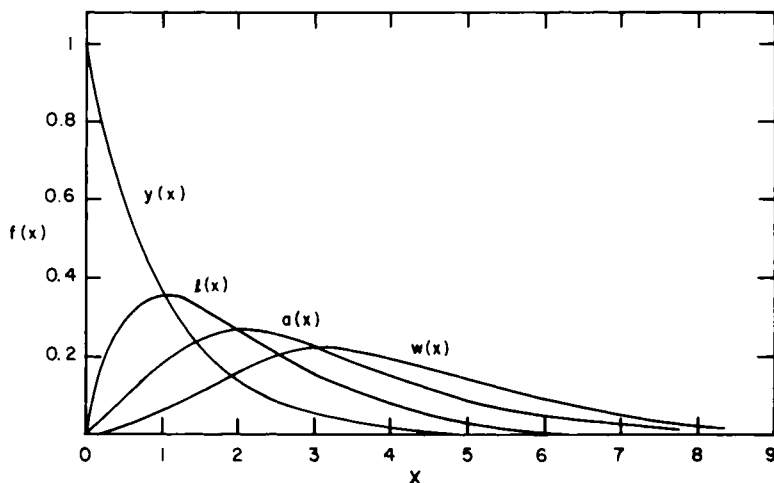


Fig. 4.4-1 Number, length, area, and mass distribution functions in a MSMPR crystallizer.

averages are the maxima (modes) on the curves shown in Fig. 4.4-1. Note that the values of these maxima are 1, 2, and 3, respectively. The definitions of these averages on a population basis, a length-weighted basis, and an area-weighted basis are given below:

$$\begin{aligned}\bar{x}_{1,0} &= \int_0^{\infty} xy \, dx / \int_0^{\infty} y \, dx \\ &= \int_0^{\infty} x \exp(-x) \, dx / \int_0^{\infty} \exp(-x) \, dx = 1\end{aligned}\quad (4.4-14)$$

$$\begin{aligned}\bar{x}_{2,1} &= \int_0^{\infty} x^2 y \, dx / \int_0^{\infty} xy \, dx \\ &= \int_0^{\infty} x^2 \exp(-x) \, dx / \int_0^{\infty} x \exp(-x) \, dx = 2\end{aligned}\quad (4.4-15)$$

$$\begin{aligned}\bar{x}_{3,2} &= \int_0^{\infty} x^3 y \, dx / \int_0^{\infty} x^2 y \, dx \\ &= \int_0^{\infty} x^3 \exp(-x) \, dx / \int_0^{\infty} x^2 \exp(-x) \, dx = 3\end{aligned}\quad (4.4-16)$$

In dimensional form, letting $x = L/G\tau$, then

$$\bar{L}_{1,0} = G\tau \quad (4.4-17)$$

$$\bar{L}_{2,1} = 2G\tau \quad (4.4-18)$$

$$\bar{L}_{3,2} = 3G\tau \quad (4.4-19)$$

From these equations, it would seem that the average size depends only on growth rate and residence time. However, as we will see later, under the constraints of the system, growth rate is intimately connected to the nucleation rate; therefore, the dominant size obtainable is determined by the kinetic rates of both phenomena.

EXAMPLE 4.4-1

From Eq. (4.4-5), the solids concentration of crystals per unit volume is $M_T = 6k_v \rho n^0 (G\tau)^4$. Following the development in Section 2.3, the mass concentration in a given size range is given by

$$dm = d \left(k_v \rho \int_0^L L^3 n dL \right) = \rho k_v L^3 n dL \quad (4.4-20)$$

The weight fraction is then dm/M_T , and thus

$$\begin{aligned} w(L) &= dW/dL = L^3 n / 6n^0 (G\tau)^4 \\ &= L^3 n^0 \exp(-L/G\tau) / 6n^0 (G\tau)^4 \end{aligned} \quad (4.4-21)$$

where dW/dL is the weight fraction distribution of crystals in suspension and is the dimensional version of Eq. (4.4-13). The maximum of the curve represented by Eq. (4.4-21) is the dominant size of the distribution. Thus, at this dominant size,

$$dW/dL = 3L^2 \exp(-L/G\tau) - (L^3/G\tau) \exp(-L/G\tau) = 0 \quad (4.4-22)$$

canceling $L \exp(-L/G\tau)$ gives

$$\bar{L}_{3,2} = L_d = 3G\tau \quad (4.4-23)$$

Thus, the mode $\bar{L}_{3,2}$ may be thought of as the dominant particle size. ◆

4.5 The Mass Balance

In Example 2.2-1, it was shown that for the distribution function (4.4-13) (which is the mass distribution function for crystal product from a MSMR crystallizer), the coefficient of variation is always 50. Consequently, the location on the size axis of this distribution can be characterized by one parameter, namely the product of the growth rate and mean residence time. Three times this parameter is the dominant particle size, which, along with the coefficient of variation, completely characterizes the distribution.

As mentioned before, the value of this parameter is related to the kinetic rates of nucleation and growth and the constraints on the system. A relationship will now be developed to show how these various factors determine the magnitude of this size parameter.

Up to this point, only the population balance has been considered. It is now necessary to incorporate a mass balance to fully define the system. The assumptions and constraints previously mentioned still apply.

The rate at which solute is lost from the mother liquor must equal the rate at which mass is gained by the solid phase. Thus,

$$Q_i C_i - Q_o C_o = Q_o M_T \quad (4.5-1)$$

Because the mass rate of phase change due to nucleation is negligibly small, the rate of make, $Q_o M_T$, can be set equal to the rate of growth on the surface of the suspended particles. Therefore,

$$\frac{1}{2} G A_T \rho V = Q_i C_i - Q_o C_o = Q_o \delta C \quad (4.5-2)$$

where $\delta C = (Q_i/Q_o) C_i - C_o$. Incorporating Eq. (4.4-4) gives

$$G = 2(\delta C) \left(\rho k_a \tau \int_0^\infty n L^2 dL \right) \quad (4.5-3)$$

We note that the concentration drop across the crystallizer depends on the retention time τ , as well as on energy inputs, for systems which operate with measurable unrelieved supersaturation. Such systems, whose yield depends on throughput, are referred to as Class I systems. In Class II systems, the exit concentration approaches C_{eq} and per-pass yield is independent of throughput. Equation (4.5-3) is valid at steady state for both Class I and Class II systems. This equation shows that the growth rate is inversely proportional to the surface area of crystals in suspension. This area is related to the size distribution by Eq. (4.4-4). The size distribution in turn is determined by the growth rate

and the nucleation rate. These rates appear in the distribution function as G and n^0 . This interrelationship forms a feedback loop which is described by Fig. 4.5-1.

We recognize that growth is a function of supersaturation, often a linear function, and therefore Eq. (4.5-3) can be written

$$s = k'(\delta C)/\tau \left(\int_0^\infty nL^2 dL \right) \quad (4.5-4)$$

where $s = C - C_{eq}$. Nucleation rate B^0 is also a function of s ; consequently n^0 can be expressed as a function of s . For a Class II system, $\delta C/\tau$ is a design choice and can be thought of as an input to the feedback loop shown as Fig. 4.5-1.

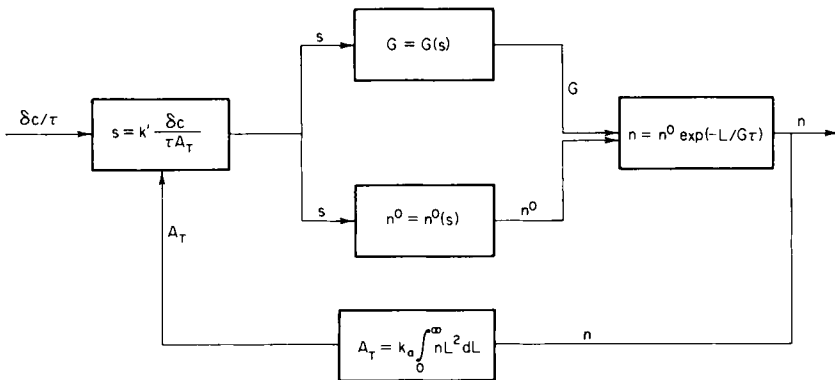


Fig. 4.5-1 Information flow diagram illustrating the interrelationship of crystal growth rate, nucleation rate, and crystal-size distribution.

In general, nucleation rate is more sensitive to supersaturation changes than is growth rate. When this is the case, the diagram shows that for longer holding times, larger and consequently fewer crystals would be expected. The net result is that G decreases less than the increase in holding time τ , with a consequent increase in dominant particle size L_d , where again, from Eq. (4.4-19), $L_d = 3G\tau$.

Higher input concentrations with an equivalent change in energy input (or removal) to produce the same final mother liquor concentration should give a larger particle size. In most cases, this does not occur. This will be considered in later chapters when homogeneous and secondary nucleation mechanisms are discussed.

4.6 Summary

This development for the MSMPR crystallizer holds for any kinetic model so long as the growth rate does not depend on size. Consequently, crystallizers of this type will give a distribution with a coefficient of variation of 50 regardless of kinetics. The relative kinetic rates of nucleation and growth will determine only the position of the distribution curve on the size axis. In terms of the one-parameter distribution function, the dominant size is a function of the relative kinetic rates and the energy and mass constraints of the system.

Deviations from the exponential distribution must be attributed to causes other than nucleation-growth rate kinetics. Special cases which apparently obtain in real systems will be discussed in later chapters, including effects of classification, poor mixing, crystal breakage, staging, and size-dependent growth. In addition, the ramification of secondary nucleation as contrasted with homogeneous nucleation will be considered.

Nomenclature

[illegible]

THE UNSTEADY STATE

Continuous crystallizers are in the main expected and designed to operate at constant conditions. Such steady-state operations are relatively easy to model when compared to batch systems, which, of course, exhibit conditions which vary in time and are consequently regarded as in the unsteady state. In the previous chapter, we exploited this steady-state nature to develop relationships showing how the process conditions and fundamental kinetic rates affect the size distribution. In this chapter, we show how the unsteady-state number and mass balances arise and how they may be used in understanding both CSD transients and CSD stability. In a later chapter, the unsteady-state nature of batch systems will be examined.

In general, most crystallizers of the MSMPR type can be readily brought to a steady-state CSD and maintained constant in that condition. This is especially true for crystallizers operating with a relatively short retention time V/Q_0 of 1 hr or less. However, there are numerous commercial crystallizers in which it is difficult or impossible to maintain CSD at a steady level. Thus, the understanding and quantitative description of CSD dynamics is a matter of no small importance. As a rule, such crystallizers exhibiting problems with CSD dynamics are designed with more complex process flows (e.g., ancillary solids segregation equipment permitting accelerated fines and/or mother liquor and/or product withdrawals) than the simple MSMPR type, and the problem of ascertaining the cause of CSD dynamics is not trivial.

At the outset, we should distinguish two types of CSD dynamics, namely

CSD *transients* and CSD *instability*. In mathematical parlance, we are referring to CSD dynamics caused by a nonhomogeneous forcing function (e.g., outside disturbance caused by perturbation in feed rate or composition, crystallizer temperature, and/or slurry withdrawal rate), or dynamics caused by the inherent instability of the characteristic equation describing CSD (excessive internal system feedback relating to the relative sensitivity of nucleation and growth rates to perturbations in the state of the system). The analyses of these two sources of CSD dynamics stem from the same dynamic population and mass balances, but proceed along different paths. Corrective actions to stabilize CSD are also different, depending on the source of CSD dynamics.

5.1 Dynamic Population Balance

We now develop the equations representing the dynamic behavior of the crystallizing system described in Chapter 4. The assumptions and constraints will be the same except that the inlet concentration and the flow rates may be functions of time. It will be assumed that the temperature, pressure, and system volume are constrained and fixed. These constraints assure that the saturation concentration of the mother liquor is fixed. In later developments, we will relax some of these requirements.

A number balance for a size range ΔL for an increment of time Δt gives: Accumulation = input – output, or

$$V \Delta n \Delta L = (Q_1 \bar{n}_i \Delta L \Delta t + V n_1 G_1 \Delta t) - (Q_0 \bar{n} \Delta L \Delta t + V n_2 G_2 \Delta t) \quad (5.1-1)$$

Rearranging and dividing by ΔL and Δt gives

$$V \Delta n / \Delta t = Q_1 n_i - Q_0 n - [V(n_2 G_2 - n_1 G_1) / \Delta L] \quad (5.1-2)$$

In the limit as ΔL and Δt approach zero, (5.1-2) becomes

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial L} + \frac{Q_0}{V} n = \frac{Q_1}{V} n_i \quad (5.1-3)$$

For a system with clear feed streams, n_i is zero. If growth rate is not a function of size, then it may be taken outside the differential. Using these conditions, (5.1-3) becomes

$$\frac{\partial n}{\partial t} + G \frac{\partial n}{\partial L} + \frac{n}{\tau} = 0 \quad (5.1-4)$$

where τ is again the drawdown or holding time in the crystallizer and may be a function of time if the feed rate is variable. The coefficient G is also a function of time.

It is instructive to simplify the macrodistributed population balance, Eq. (3.5-10), to obtain the same results for CSD dynamics in a MSMPR-type crystallizer:

$$\partial n / \partial t + \nabla \cdot \mathbf{v}_i n + n d(\log V) / dt = B - D - \sum_k (Q_k n_k / V)$$

Assuming a one-dimensional particle distribution, the internal velocity vector $\mathbf{v}_i$ is simply the particle linear growth rate G . Thus,

$$\nabla \cdot \mathbf{v}_i n = \frac{\partial}{\partial L} (Gn) = G \frac{\partial n}{\partial L} \quad (5.1-5)$$

assuming $G \neq G(L)$, i.e., McCabe's ΔL law holds. If negligible fracture of particles occurs, with possible attrition included as an increased net density of nuclei at a vanishingly small size, the birth and death terms can be taken as zero. Thus,

$$B = D = 0 \quad (5.1-6)$$

One inlet stream is assumed, with flow Q_i and distribution n_i , with one mixed discharge stream Q_o with representative distribution n . Thus, the slurry input and output term becomes

$$-\sum_k Q_k n_k = Q_i n_i - Q_o n \quad (5.1-7)$$

If clear liquor feeds are assumed ($n_i = 0$), the macro-distributed population balance reduces to

$$\frac{\partial n}{\partial t} + n \frac{d(\log V)}{dt} + G \frac{\partial n}{\partial L} + \frac{n}{\tau} = 0 \quad (5.1-8)$$

where again $V/Q_o = \tau$. The difference between Eqs. (5.1-4) and (5.1-8) is the term $n d(\log V)/dt$ in the latter equation. At this point, we must come to grips with the basis on which the population density is defined. Thus, the two choices discussed in Chapter 3 are

$$n [=] \text{ number}(\text{length})^{-1} (\text{volume of slurry})^{-1} \quad (5.1-9)$$

$$n [=] \text{ number}(\text{length})^{-1} (\text{volume mother liquor})^{-1} \quad (5.1-9')$$

A completely equivalent description of a particulate process can be made with either definition, but the basis must be specified. If n is defined on a mother liquor basis, then V is the volume holdup of clear liquor which changes as the suspension density (i.e., void fraction) changes, even when total system volume remains constant. Equation (5.1-4) was derived on the basis of suspension volume and hence $d(\log V) = 0$ assuming constant total volumetric holdup. If these two bases are to be completely equivalent, there must obviously be other compensating terms if the two describing equations are different. This difference comes about in the description of the nucleation rate. Thus, as normally defined,¹

$$B^0 = \text{nuclei}(\text{time})^{-1} (\text{volume of mother liquor})^{-1} \quad (5.1-10)$$

and in the case of n based on slurry volume given by Eq. (5.1-4), the expression for B^0 must be corrected for the changing void fraction. There are two cases of CSD dynamics where the basis for n becomes immaterial and the simpler equation, (5.1-4), together with (5.1-10), can be used:

a. Thin slurries where $d(\log V)/dt \approx 0$. This is probably the normal case in crystallization practice, as the void fraction ε might normally be greater than 0.8.

b. A Class II MSMPR crystallizer with constant feed concentration, where solids concentration remains invariant in the presence of dynamic CSD.

We note that a Class II (high-yield) crystallizer is defined as one where negligible accumulation of solute as supersaturation can occur. Hence, with constant feed concentration and nonselective removal as a function of size, the solids in the magma must remain constant, independent of CSD dynamics.

We return to our example of dynamics of CSD in a MSMPR crystallizer with a Class II crystal system, taking note of the simplification thus resulting from point (b) above to drop the $n d(\log V)/dt$ term, reducing (5.1-8) identically to (5.1-4).

At this point, we must combine Eq. (5.1-8) with a dynamic mass balance, which will be shown to reduce, for a Class II system, to a constraint on the growth rate. Thus, accumulation = input - output + generation, for total solute, solid phase plus supersaturation, in the system:

$$V \frac{d}{dt} (M_T + C) = Q_i C_i - Q_o C - Q_o M_T \quad (5.1-11)$$

¹ It has always seemed reasonable to express nucleation rate on a mother liquor basis, but recent work confirming the importance of secondary nucleation mechanisms occurring on or near the crystal surface makes the logic of this choice less obvious.

Recognizing that in a Class II system at constant temperature, $dC/dt = 0$, then Eq. (5.1-11) becomes

$$V dM_T/dt = Q_i C_i - Q_o C - Q_o M_T \quad (5.1-12)$$

The right-hand side of (5.1-12) satisfies the steady-state relationship

$$Q_i C_i - Q_o C - Q_o M_T = 0 \quad (5.1-13)$$

Hence, $dM_T/dt = 0$ for a Class II system with steady feeds, as indicated previously. We further note that changes in flow (assuming constant volumetric holdup in the vessel) act uniformly on all members of (5.1-13), while changes in C_i and C affect different terms. Thus, for the Class II MSMPR crystallizer, time-dependent feed concentration and solubility levels (temperature levels) will perturb solids concentration but dynamic flow rates will not. Size classification of solids will interact with dynamic flows and CSD to perturb the solids concentration, and hence the above statement is only true for the MSMPR case.

Having only demonstrated the constancy of the total solids concentration with an overall dynamic mass balance, we next turn to a solute balance. Thus, accumulation = flow input – flow output – rate of make, or

$$0 = Q_i C_i - Q_o C - V \rho k_a \int_0^\infty (G/2) n L^2 dL \quad (5.1-14)$$

Rearranging gives

$$\int_0^\infty G n L^2 dL = 2(Q_i C_i - Q_o C)/V \rho k_a = 2 \delta C / \tau \rho k_a \quad (5.1-15)$$

Assuming McCabe's ΔL law holds, a suitable constraint on the linear growth rate becomes [Eq. (4.5-3)]

$$G = 2 \delta C / \left(\rho k_a \tau \int_0^\infty n L^2 dL \right)$$

Equation (4.5-3) holds for all Class II systems regardless of whether flows and concentrations are constant or whether product removal is size-classified. For a Class II MSMPR crystallizer or for steady state in any system, production rate P can be equated to the drop in solute concentration times the flow across the vessel. Thus, the constraint on growth rate can be written as

$$G = 2 \delta C / \left(\tau \rho k_a \int_0^\infty n L^2 dL \right) = 2(P/Q_o) / \left(\tau \rho k_a \int_0^\infty n L^2 dL \right) \quad (5.1-16)$$

This relationship provides the informational feedback unique to crystallization, allowing a large measure of self-regulation for CSD. Note that the integral is the second moment of the distribution and is therefore proportional to the transient surface area of the crystals. This equation is identical to Eq. (4.5-3) derived for the steady state except that δC and n may be functions of time. Figure 5.1-1 illustrates this dynamic information feedback represented by Eq. (5.1-16), which regulates CSD and, for certain kinetic regions, can over-regulate the process, causing CSD instability.

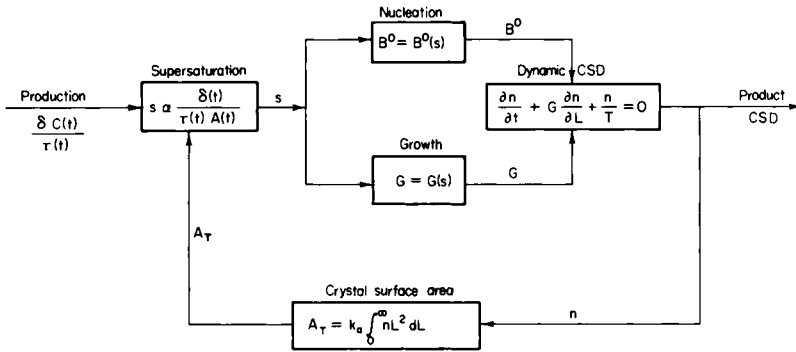


Fig. 5.1-1 Information block diagram showing internal CSD self-regulation feedback loop. Other feedback loops regulating secondary nucleation may exist.

In order to obtain a boundary condition for the distribution, it is necessary to introduce a kinetic model for nucleation. For simplicity, we use a model which assumes nucleation is given by a power-law relationship with supersaturation,²

$$B^0 = k_N s^i \quad (5.1-17)$$

where s is the concentration in excess of the saturation concentration, divided by the saturation concentration. For growth a linear function of supersaturation, we get

$$B^0 = k_N' G^i \quad (5.1-18)$$

² Other models could be used, including the Miers or Volmer models, or one may relate the secondary effects directly to the suspension density or suspension area. Note that the area term is nested in G as per Eq. (5.1-16) and thus it is somewhat redundant to independently factor out the area term. It is difficult to prove or disprove secondary nucleation mechanisms as being area-dependent from MSMPR data. See Chapter 6 for a more complete discussion of secondary nucleation kinetics models. If secondary nucleation kinetics indeed depend on specific surface area, mass, or higher moments of the distribution, then additional information feedbacks must be included in Fig. 5.1-1.

However, by the definition of the population density of nuclei,

$$B^0 = n^0 G \quad (5.1-19)$$

Therefore,

$$n(t, 0) = n^0(t) = k_N' G(t)^{i-1} \quad (5.1-20)$$

Equation (5.1-20) provides the necessary boundary condition and (5.1-4), (5.1-16), and (5.1-20) can be solved together with an initial condition to describe CSD transients or test for CSD stability.

5.2 CSD Transients

The initial condition is whatever function describes the distribution at $t = 0$. If the system has been previously operating at steady state, then

$$n(0, L) = n_0^0 \exp(-L/G_0 \tau) \quad (5.2-1)$$

where the subscript indicates the condition during the steady-state operation.

Adding Eq. (5.2-1) to the previous set provides a description of the transient behavior of the size distribution and these equations may be solved numerically.

The solution of the above set is quite difficult, and is impossible if the constants are not known, which is the case for most systems. However, by casting the system in dimensionless form, the effect of disturbances can be demonstrated. Letting the subscript zero denote initial steady-state values, we define

$$\begin{aligned} L/G_0 \tau_0 &= x, & t/\tau_0 &= \theta, & G(t)/G_0 &= \rho(\theta) \\ \delta C(t)/C_0 &= \sigma(\theta), & Q_0/Q(t) &= \tau(\theta), & M_T(t)/M_{T_0} &= f_3(\theta) \\ A_T(t)/A_{T_0} &= f_2(\theta), & n(t, L)/n_0^0 &= y(\theta, x) \end{aligned} \quad (5.2-2)$$

Using these definitions, the set (5.1-4), (5.1-16), (5.1-20), and (5.2-1) becomes

$$\frac{\partial y}{\partial \theta} + \rho \frac{\partial y}{\partial x} + \frac{y}{\tau} = 0 \quad (5.2-3)$$

$$\rho = \sigma/\tau f_2 \quad (5.2-4)$$

$$y^0 = \rho^{i-1} \quad (5.2-5)$$

$$y_0 = \exp(-x) \quad (5.2-6)$$

EXAMPLE 5.2-1

For a system where $i = 4$, find the time-varying behavior of the size distribution after a threefold increase in feed rate. Assume the system is initially at steady state at the lower feed rate.

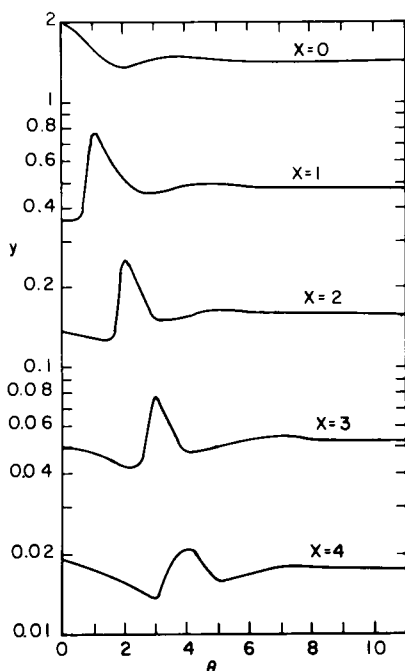


Fig. 5.2-1 Calculated dynamic response of Class II MSMPR dimensionless population density to threefold increase in feed rate; $i = 4$ [after A. D. Randolph and M. A. Larson, *AIChE J.* **8**, 369 (1962)].

A finite-difference scheme is used with $\sigma = 1$ and $\tau = \frac{1}{3}$. The results for various dimensionless sizes are shown in Fig. 5.2-1. Observe how the showers of nuclei formed at $\theta = 0^+$ grow down the size range as time passes.

Figure 5.2-2 shows the experimental transient CSD behavior of an ammonium sulfate cooling crystallizer. Note the same qualitative behavior. The fines transients die out quickly, indicating the CSD is basically stable. The initial shower grows through the size range, perturbing the CSD at larger sizes over a long period of time. ♦

5.3 Transient Moment Equations

The above set is very difficult to solve numerically and becomes almost impossible if i is greater than 6 or 7. In addition, it is difficult to study the stability of the system working with the partial differential equation. To avoid

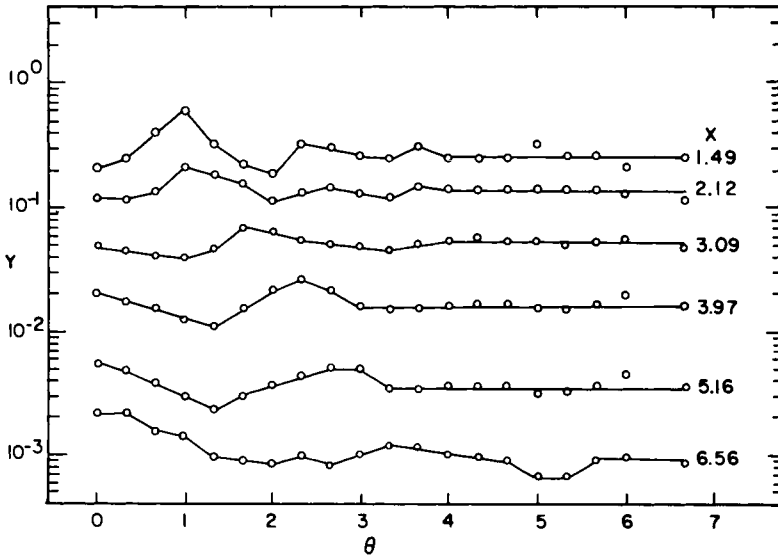


Fig. 5.2-2 Experimental dynamic response of population density to feed-rate increase for ammonium sulfate system (after C. W. Chambliss, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1966, unpublished).

these problems, it is only necessary to cast the set in terms of the moment equations.

Again define the j th moment of the dimensionless distribution as

$$\mu_j = \int_0^\infty y x^j dx, \quad j = 0, 1, 2, 3, 4 \quad (5.3-1)$$

As noted before, only the first four moments have physical significance, being related to the total number, length, area, and mass, respectively. It turns out that it is only necessary to work with these four moments to adequately define the system.

For simplicity, we define the normalized dimensionless moments as

$$f_j = \mu_j(\theta)/\mu_j(0) = \int_0^\infty y(\theta) x^j dx / \int_0^\infty y_0 x^j dx \quad (5.3-2)$$

From Chapter 4, we note that the denominator of (5.3-2) for the first four moments is 1, 1, 2, and 6, respectively. Therefore,

$$f_j = \left(\int_0^\infty y(\theta) x^j dx \right) / j! \quad (5.3-3)$$

Multiplying Eq. (5.2-3) by dx and integrating gives³

$$\int_0^\infty (\partial y / \partial \theta) dx + \rho \int_0^\infty dy + (1/\tau) \int_0^\infty y dx = 0 \quad (5.3-4)$$

or

$$(d\mu_0/d\theta) - \rho y^0 + (\mu_0/\tau) = 0 \quad (5.3-5)$$

Using Eqs. (5.2-4), (5.2-5), and (5.3-3) in (5.3-5) gives

$$df_0/d\theta + f_0/\tau = (\sigma/\tau f_2)^i \quad (5.3-6)$$

Similarly, using the definition of normalized moments 1, 2, and 3, one obtains

$$df_1/d\theta + f_1/\tau = f_0 \sigma / \tau f_2 \quad (5.3-7)$$

$$df_2/d\theta + f_2/\tau = f_1 \sigma / \tau f_2 \quad (5.3-8)$$

$$df_3/d\theta + f_3/\tau = \sigma / \tau \quad (5.3-9)$$

The set of equations (5.3-6)–(5.3-9) is a closed set of nonlinear ordinary differential equations with initial conditions of unity. In addition, the steady-state values of σ and τ are also unity. It is not possible to find an analytic

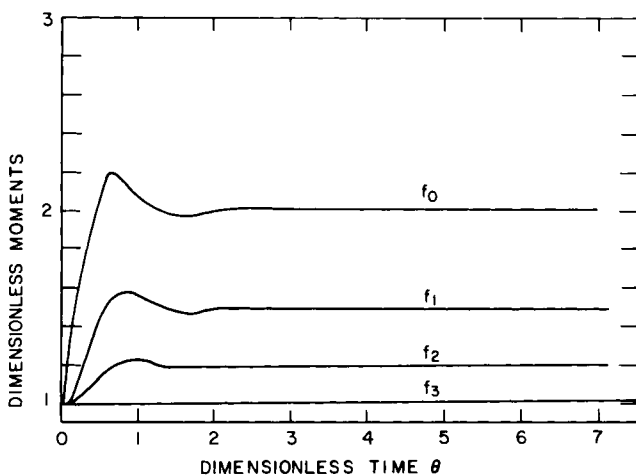


Fig. 5.3-1 Transient response of the CSD moments for a step change in holding time.

³ Alternately, we could have simplified and made dimensionless substitutions in the macro-moment population balance, Eq. (3.7-3).

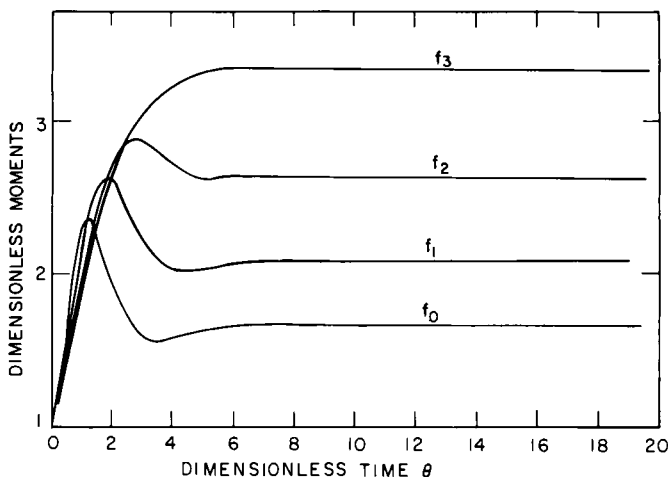


Fig. 5.3-2 Transient response of the CSD moments for a step change in rate of make.

solution to this set, but it can be solved on an analog computer with sufficient nonlinear elements.

For upsets in feed rate, τ becomes a function of time and the first three equations define the dynamics of the system. If the feed concentration is a variable, σ becomes time-varying and it is necessary to use all four equations to define the dynamics. Some typical responses to step changes in dimensionless residence time τ and production rate σ are shown in Figs. 5.3-1 and 5.3-2. Note that as residence time is shortened, more particles are formed, and more area is formed. This result is of course a function of the crystal nucleation-growth kinetics. Experimental moments are difficult to determine because it is not possible to enumerate all crystals to zero size.

These same moment equations will be used in a subsequent section to study the stability of CSD.

5.4 Transient Size Distribution by Method of Characteristics

The numerical solution of Eq. (5.2-3) is extremely difficult when the order of nucleation is high. One alternate procedure utilizes the set of moment equations to affect a semianalytic solution.

We define a new function $\Psi(\theta)$ as

$$\Psi = \int_0^\theta \rho(p) dp \quad (5.4-1)$$

By the method of characteristics, the solution of Eq. (5.2-3) is in two parts:

$$y_1 = [\exp(-\theta/\tau)] [y^0(\theta) \exp(\theta'/\tau)]$$

$$\text{where } \theta' = \Psi^{-1}[\Psi(\theta) - x] \quad \text{for } x < \Psi(\theta) \quad (5.4-2a)$$

and

$$y_2 = [\exp(-\theta/\tau)] [y_0(x')]$$

$$\text{where } x' = [x - \Psi(\theta)] \quad \text{for } x \geq \Psi(\theta) \quad (5.4-2b)$$

where $y^0(\theta)$ is defined by Eq. (5.2-5),

$$y^0(\theta) = \rho^{i-1} = [\sigma/\tau f_2]^{i-1}$$

and $y_0(x')$ is given from Eq. (5.2-6),

$$y_0(x') = \exp(-x') = \exp\{-[x - \Psi(\theta)]\}$$

In order to calculate the population transients such as those in Fig. 5.2-1 one first solves the set of moment equations (5.3-6)–(5.3-9) on an analog computer as well as Eq. (5.4-1).

These analog solutions together with Eqs. (5.4-2a, b) can now be used to obtain the transient population densities of various sizes in the size range (see Appendix C).

Another semianalytic technique for the solution of (5.2-3) would be to solve the moment equations up to, say, f_8 or f_{10} and then recover the distribution from the matrix representation of the leading moments, Eqs. (3.8-10) and (3.8-11). If the normalized moments $\mathbf{f}$ are used in place of the moment vector $\mathbf{m}$ in (3.8-10), then a suitably normalized definition for the coefficients $a_{j,k}$ must be substituted for Eq. (3.8-11). Thus,

$$a_{j,k} = (x_k)^j \Delta x_k / j! \quad (5.4-3)$$

form the dimensionless coefficients. The matrix representation of the normalized moments is then given as

$$\mathbf{f}(\theta) = \mathbf{A}\mathbf{y} \quad (5.4-4)$$

Corresponding values of n at L are found from y at x using the original dimensionless transformations discussed in Section 5.2.

5.5 Stability of CSD

The feedback loop shown in Fig. 5.1-1 acts as an effective means of self-regulation for the CSD produced in a continuous crystallizer. As with all feedback regulator controls, if the feedback is excessive, the system will over-react to changes, and ultimately become unstable, i.e., exhibit sustained oscillations independent of outside disturbances.

The stability of CSD can be analyzed at several levels of complication; however, the approach is essentially the same regardless of the level of sophistication. Stability of CSD in an arbitrary mixed volume is defined by the transient macrodistributed population balance [see Eq. (3.5-10)]

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial L}(Gn) + n \frac{d(\log V)}{dt} = B - D - \sum_k \frac{Q_k n_k}{V}$$

with auxiliary solute mass balance and system kinetics

$$V ds/dt = Q_i C_i - Q_o C - \rho k_a V \int_0^\infty (G/2)nL^2 dL \quad (5.5-1)$$

$$B^0 = B^0(s, n) \quad (5.5-2)$$

and

$$G = G(s) \quad (5.5-3)$$

Equation (5.5-2) recognizes that nucleation may be by secondary mechanisms and would therefore be a function of the distribution n . If the above set of equations admits of a steady, nonoscillating solution for any system disturbance of finite duration, the CSD in the mixed suspension V is stable. Note that such a definition considers nonlinear limit cycles of CSD as unstable operation. More particularly, if the roots of the characteristic equation of the linearized system equations all have negative real parts, the system is considered to be stable to small perturbations around a steady operating condition.

Numerous simplifications of Eqs. (3.5-10) and (5.5-1)–(5.5-3) are made before proceeding with a stability analysis. As discussed in Section 5.1, $dC/dt \cong 0$ for a Class II system and the instantaneous dynamic relationship (5.1-16),

$$G = 2(P/Q_o) / \left(\tau \rho k_a \int_0^\infty nL^2 dL \right)$$

may be substituted for Eqs. (5.5-1) and (5.5-3). There is only a quantitative

difference in stability between Class I systems operating with a reasonable crystal yield and Class II systems; the latter type is certainly easier to analyze and is perhaps just as instructive, so only Class II systems will be considered in the subsequent analysis. However, size-dependent crystal removal has a strong effect through the CSD equations and perhaps even qualitative differences in CSD stability may occur for extremes in particle classification [1]. Such changes in removal rate as a function of size render nonconstant the size distribution equations' coefficient in the variable L and make a rigorous stability analysis difficult at best.

The stability of CSD in a Class II MSMPR system with a point fines trap is simple, yet instructive, and will be discussed in detail. A point fines trap is defined as a fines-removal system in which the excess particles are segregated and removed at a size vanishingly small compared to the resultant product crystal size.

The appropriate CSD equations, in dimensionless normalized form, may be written for this system as

$$\begin{aligned} df_0/d\theta + f_0 &= \rho y^0 \\ df_1/d\theta + f_1 &= \rho f_0 \\ df_2/d\theta + f_2 &= \rho f_1 \end{aligned} \quad (5.5-4)$$

with the growth rate constraint giving

$$\rho = 1/f_2 \quad (5.5-5)$$

and with generalized nucleation-growth rate kinetics

$$n_{\text{net}}^0 = \exp(-\lambda) n^0(G) \quad (5.5-6)$$

or in dimensionless form,

$$y^0 = \exp(\lambda_0 - \lambda) n^0/n_0^0 \quad (5.5-6')$$

where $\lambda = L_F Q_F/GV$ is the exponential decay ratio of the original nuclei, with Q_F and L_F the removal rate and maximum size of the fines, respectively. Decay ratios of 5–7 are not uncommon with excessive dissolving, indicating perhaps one out of a thousand original nuclei are left to grow as product.

These moment equations are linearized about their steady-state values by writing

$$f_j = 1 + \tilde{f}_j, \quad \rho = 1 + \tilde{\rho}, \quad y^0 = 1 + \tilde{y}^0 \quad (5.5-7)$$

where the tilde indicates a deviation from steady state.

This yields the linearized set

$$\begin{aligned} d\tilde{f}_0/d\theta + \tilde{f}_0 &= \tilde{\rho} + \tilde{y}^0 \\ d\tilde{f}_1/d\theta + \tilde{f}_1 &= \tilde{\rho} + \tilde{f}_0 \\ d\tilde{f}_2/d\theta + \tilde{f}_2 &= \tilde{\rho} + \tilde{f}_1 \end{aligned} \quad (5.5-8)$$

Equation (5.5-5) can be linearized with a Taylor expansion to give the first-order approximation

$$\tilde{\rho} = -\tilde{f}_2 \quad (5.5-9)$$

and similarly from Eq. (5.5-6')

$$\tilde{y}^0 = (dy^0/d\rho)|_{\rho=\rho_0, \lambda=\lambda_0} \quad (5.5-10)$$

Substituting (5.5-9) and (5.5-10) in set (5.5-8) and Laplace-transforming with zero initial conditions gives

$$\begin{aligned} F_0[s+1] + [(dy^0/d\rho)|_{\rho_0, \lambda_0} + 1] F_2 &= 0 \\ -F_0 + F_1[s+1] + F_2 &= 0 \\ -F_1 + F_2[s+2] &= 0 \end{aligned} \quad (5.5-11)$$

where s is the Laplace operator.

The characteristic equation for this set of transformed, linear, homogeneous differential equations is found to be

$$s^3 + 4s^2 + 6s + 4 + (dy^0/d\rho)|_{\rho_0, \lambda_0} = 0$$

Applying the Routh stability criterion to this characteristic equation gives the criterion for stability of CSD in terms of nucleation-growth rate kinetics as

$$(dy^0/d\rho)|_{\rho_0, \lambda_0} < 20 \quad (5.5-12)$$

Differentiating (5.5-6') gives the stability relationship in terms of the dissolving parameter λ_0 and nucleation kinetics. Thus,

$$[d(\log n^0)/d(\log G)]|_{n_0^0, G_0} < 20 - \lambda_0 \quad (5.5-13)$$

where the derivative is evaluated at the steady-state conditions. Recognizing that $B^0 = Gn^0$ yields an equivalent stability criterion in terms of nucleation rate. Thus,

$$[d(\log B^0)/d(\log G)]|_{B_0^0, G_0} < 21 - \lambda_0 \quad (5.5-14)$$

For an MSMPR crystallizer with no dissolving, $\lambda_0 = 0$, and the well-known criterion

$$[d(\log B^0)/d(\log G)]|_{B_0^0, G_0} < 21 \quad (5.5-14')$$

results.

EXAMPLE 5.1-1

Discuss the stability criterion (5.5-14') in the context of power-law, Miers, and Volmer nucleation kinetic models.⁴

a. For a Class II system, power-law nucleation kinetics can be written as $B^0 = k_N G^i$ and stability is guaranteed by

$$[d(\log B^0)/d(\log G)]|_{B_0^0, G_0} = i < 21 \quad (5.5-15)$$

Secondary nucleation mechanisms seldom result in power-law exponents i greater than three or four, and in regions where such secondary mechanisms are operative, the MSMPR crystallizer is unconditionally stable. The value of 21 represents such an extreme kinetic order that the criterion can be thought of as a discontinuity in nucleation rate given by crossing the threshold of an operative nucleation mechanism. It is interesting to note that in the dozen or so MSMPR kinetic studies which support the power-law form of kinetics, no CSD instability has been reported.

b. Miers kinetics can be stated as

$$\begin{aligned} B^0 &= k_N (G - G_m)^i, & G > G_m \\ B^0 &= 0, & G < G_m \end{aligned} \quad (5.5-16)$$

for a Class II system, where G_m is the value of growth rate at a metastable level of driving forces where nucleation begins. Applying the stability criterion to these kinetics yields

$$[d(\log B^0)/d(\log G)]|_{B_0^0, G_0} = [G_0/(G_0 - G_m)] i < 21 \quad (5.5-17)$$

It is obvious that as the point of operation G_0 , decreases toward the metastable level G_m , the stability criterion is exceeded and an unstable CSD results. Such instability could be prevented by increasing the throughput of the system, thus raising the driving forces sufficiently above the metastable threshold. Miers-type kinetics could explain the cyclic behavior of CSD observed in some industrial crystallizers with long retention times, but again, such behavior has not been reported in bench-scale MSMPR units covering a wider range of driving forces.

⁴ See Chapter 6 for discussion of nucleation-growth rate kinetic models.

c. Volmer kinetics can be stated for a Class II system as

$$B^0 = k_1 \exp[-k_2/\log^2(1+k_3 G)] \quad (5.5-18)$$

where it is assumed that growth rate is a linear function of supersaturation. Applying the stability criterion to (5.5-18) gives

$$\left. \frac{d(\log B^0)}{d(\log G)} \right|_{B_0^0, G_0} = \frac{2k_2 k_3 G_0}{(1+k_3 G_0) \log^3(1+k_3 G_0)} < 21 \quad (5.5-19)$$

Volmer kinetics are qualitatively the same as Miers kinetics for low driving forces. As the growth rate G_0 at the steady operating point approaches zero, the criterion is exceeded and CSD instability is predicted. As with Miers-type kinetics, this instability could be eliminated by forcing the throughput, thus raising the system driving forces. ♦

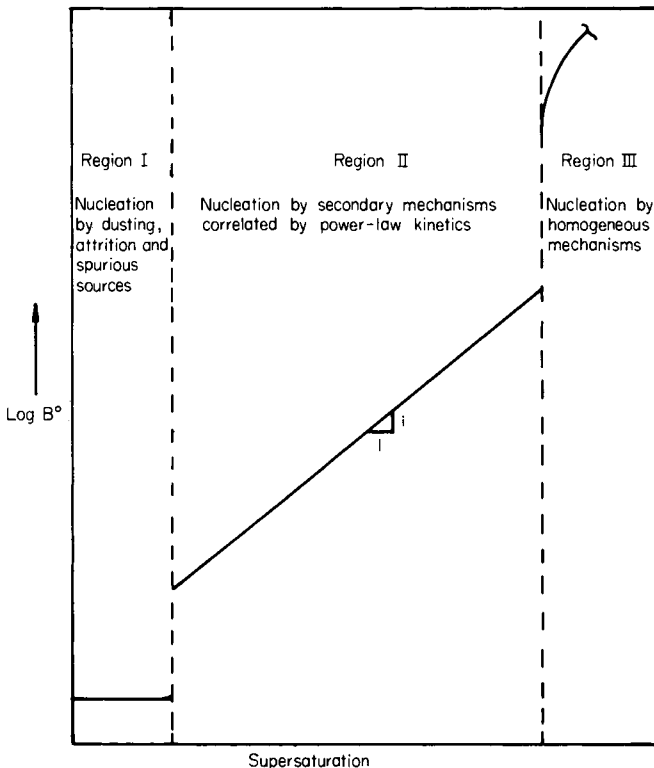


Fig. 5.5-1 Hypothetical nucleation-growth-rate plot showing discontinuous regions causing CSD instability in an MSMPR crystallizer.

In all of the three cases discussed in Example 5.5-1, it should be remembered that the instabilities predicted were essentially at discontinuities of the nucleation function. *For the Miers and Volmer models, instability was predicted at the lower threshold of nucleation at low supersaturations.* In fact, if such discontinuities exist, they should be experimentally measurable and should appear as finite discontinuities in a $\log B^0$ versus $\log G$ plot (see Fig. 5.5-1) obtained from interpretation of MSMPR data.

Instability in industrial crystallizers, when it occurs, is usually associated with extremely long solids retention times, and/or ancillary solids removal systems, and/or excessive fines destruction, and/or systems exhibiting very small levels of stable supersaturation. Thus, it is difficult, it not impossible, from the idealized analysis of the Class II MSMPR crystallizer to pinpoint the source of difficulty. A further difficulty in explaining CSD instability with the Miers and Volmer models is that instability is often observed with high rather than low driving forces when excessive fines dissolving forces the supersaturation to high levels. However, it is possible to explain this apparent anomaly. Secondary low-order mechanisms of nucleation predominate at supersaturations less than the threshold limits predicted by the Miers and Volmer models. The stability criterion can be exceeded when the suddenly appearing homogeneous nucleation predicted by the Miers and Volmer models, added to nucleation produced by secondary mechanisms, causes an essential discontinuity in total nucleation rate. Thus, if secondary nucleation can be represented by power-law kinetics, the total nucleation rate is given as

$$B^0 = k_N G^i + k_1 \exp[-k_2/\log^2(1 + k_3 G)] \quad (5.5-20)$$

and a log derivative,

$$[d(\log B^0)/d(\log G)]|_{B_0^0, G_0}$$

greater than 21 can occur at a relatively large value of G , depending on the values of the parameters. The metastable limit would then be properly described as an upper level of supersaturation where a rapid increase in total nucleation occurred due to the beginning of homogeneous nucleation, rather than a lower limit of supersaturation where all nucleation ceased. Conceivably, there exists a truly lower metastable limit below which even secondary nucleation ceases and crystal grain is only generated by breakage, dusting, and spurious sources. Such hypothetical upper and lower discontinuities in nucleation rate, shown in Fig. 5.5-1, could explain instability with both excessive fines removal and extremely long retention times.

The contradictory effects of fines dissolution on CSD instability can be observed from the above discussion. Raising the supersaturation driving forces by fines destruction could, in principle, move the system away from a Miers-

type lower metastable point, thus stabilizing the system. Alternately, the driving forces could be forced toward an upper metastable threshold of homogeneous nucleation, thus causing instability. Such anomalous nucleation behavior should be detected from laboratory MSMPR kinetic studies. Much light could be shed on the problem of CSD instability if a bench-scale MSMPR unit could be operated as a CSD oscillator.

A further apparent anomaly of fines destruction is that fines removal narrows the stable region, as shown by Eq. (5.5-13), while in fact (depending on the mode of recycling dissolved fines), transient CSD response from system upsets is greatly improved due to accelerated removal of the excursions of nuclei. In long-holding-time crystallizers, it is sometimes difficult to distinguish CSD

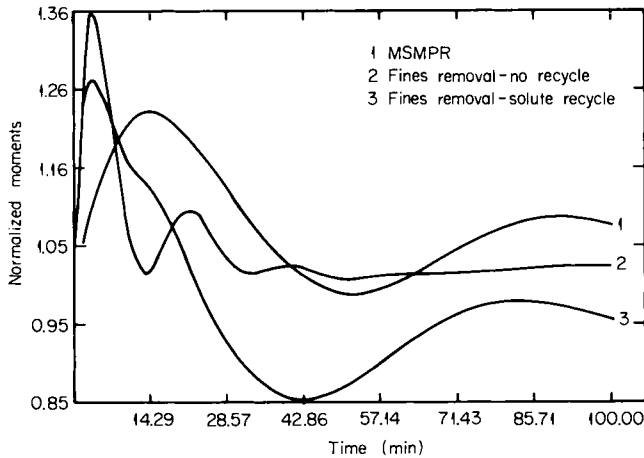


Fig. 5.5-2 Response of dimensionless total crystal population to step increase in production rate [after H. E. Nuttall, Ph.D. Thesis, University of Arizona, Tucson, Arizona, 1971, unpublished].

transients from CSD instability, thus making difficult an unambiguous judgement on whether fines removal is an asset or detriment to CSD dynamics in such a system. Figure 5.5-2 plots the dimensionless total crystal population (normalized zeroth moment) after a step change in production rate for a Class II system operating with a mean retention time of 20 min and with nucleation sensitivity parameter $i = 5$. Curve 1 represents the MSMPR case, while curves 2 and 3 represent the same system with a distributed fines trap removing fines at a size representing a significant fraction ($\sim 20\%$) of the total production rate and with advance or dissolving and recycle of these fines, respectively. Curve 2 illustrates the excellent improvement in transient response that is expected with fines removal if the solute resources represented by fines removal are not recycled. Such performance could be obtained by

recycling fines to crystallizer feed and maintaining constant feed composition and/or dissolving fines at a smaller size but higher withdrawal rate, in which case, the fines would represent a negligible fraction of solute resources. Curve 3 illustrates that when an appreciable mass fraction of dissolved fines are recycled, negligible improvement in transient response to system upsets is obtained. It should be pointed out that the CSD's and hence zeroth moments are quite different in each of these three cases; thus, the above comments were based on response time and not absolute values of these dimensionless moments.

Classified product removal results in poorer transient response characteristics as well as a lowering of the stability region. (As mentioned previously in this chapter, idealized classification, represented by no particle removal up to

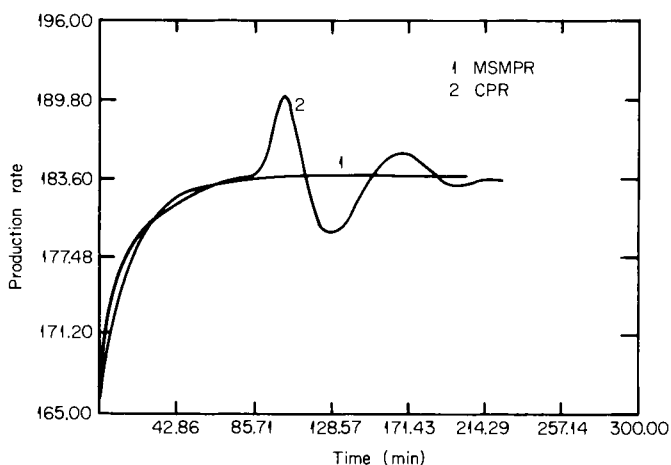


Fig. 5.5-3 Dynamic response of production rate after a 10% increase in solute resources with and without classified product removal [after H. E. Nuttall, Ph.D. Thesis, University of Arizona, Tucson, Arizona, 1971, unpublished].

product size and immediate removal at that size, severely unstabilizes CSD. More realistic classification models in which mixed removal occurs up to product size with accelerated removal thereafter result in a variable-coefficient dynamic population balance which is extremely difficult to analyze for stability.) Figure 5.5-3 illustrates the detrimental effect of classified product removal on CSD transient response for the same system shown in Fig. 5.5-2. These curves plot the dynamic response of production rate after a 10% increase in solute resources. Curve 1 represents the MSMPR case and curve 2 represents classified product removal.

Finally, it is not at all apparent that all of the information feedbacks have been included in CSD stability analyses reported to date. Ancillary removal streams may have been modeled at too elementary a level, i.e., their operation

may itself depend on the dynamic CSD, or additional secondary nucleation feedbacks may have been omitted. Secondary nucleation studies⁵ indicate that such nucleation depends on both the surface area and mass of the individual crystals which act as sites for secondary nucleation. Thus, secondary nucleation might reasonably correlate with higher moments of the distribution. Analysis of CSD stability in such a case would involve no conceptual complications but would require higher moments to be taken in the analysis.

5.6 Summary

CSD stability and transients were both described by coupling the dynamic population and mass balances together with empirical nucleation–growth rate kinetics. The form of the dynamic mass balance, and hence the complexity of the resulting set of equations, differs for Class I (variable-yield) and Class II (high-yield) systems. Transients and stability of CSD are only quantitatively different in these two types of systems and Class II systems were used as illustration.

CSD transients can only be evaluated meaningfully if external disturbances are well-characterized. In typical industrial crystallization practice, no attempt is made to control CSD transients other than to minimize system upsets. The theory of CSD transient behavior presented in this chapter should be of benefit if quantitative simulation is used to attempt compensation for such known disturbances.

CSD stability was shown to depend on the relative kinetic sensitivity of nucleation and growth rates when both are given as kinetic functions of the crystallization driving forces (supersaturation). Analysis indicates that the MSMR crystallizer is very stable; only operation near an essentially discontinuous change in nucleation rate can cause CSD cycling. Fines removal improves transient CSD response to disturbances while somewhat narrowing the stable operating range relative to the MSMR case. Severe product classification greatly lowers the CSD stability range relative to the MSMR case and results in large swings in solids concentration and production rate.

Information feedback due to secondary nucleation kinetics has not been included in CSD stability analyses. Such additional secondary nucleation feedback could exert a profound influence on crystallizer stability, especially if such secondary effects are coupled with size-dependent product removal.

⁵ Unpublished data on K_2SO_4 system, M. D. Cise and A. D. Randolph, University of Arizona.

Nomenclature

A	Specific crystal surface area in suspension	$\mathbf{v}_i$	Particle velocity along internal coordinates
$B(L)$	Crystal birth function at size L	x	Dimensionless crystal size
B^0	Crystal nucleation rate	GREEK SYMBOLS	
C	Solute concentration	θ	Dimensionless time
$D(L)$	Crystal death function at size L	λ	Dimensionless fines-dissolving parameter
$f_j(\theta)$	Normalized j th moment of dimensionless population distribution	$\mu_j(\theta)$	j th moment of dimensionless population density
$\tilde{f}_j(\theta)$	Perturbation in j th dimensionless normalized moment	ρ	Crystal density
G	Linear crystal growth rate	$\rho(\theta)$	Ratio of dynamic growth rate to steady-state value
i	Nucleation sensitivity parameter	$\sigma(\theta)$	Ratio of dynamic solute concentration to steady-state value
k_N	Constant in nucleation kinetics equation	$\tau(\theta)$	Ratio of steady-state to dynamic exit suspension flow rate
k_a	Crystal shape factor	τ	Retention time
L	Crystal size	SUBSCRIPTS	
M	Specific crystal mass in suspension	i	Inlet stream
n	Crystal population density	k	k th stream
n^0	Nuclei population density	o	Outlet stream or steady-state value
P	Crystal production rate	T	Total quantity
Q	Volumetric flow rate		
s	Supersaturation as $C - C_{eq}$		
V	Suspension volume		

Reference

1. M. Sherwin, R. Shinnar, and S. Katz, *Chem. Eng. Progr. Symp. Ser.* 95 **65**, 75 (1969).

CRYSTALLIZATION KINETICS

Nucleation and crystal growth were described by Gibbs as discontinuous changes of phase which are large in degree but at least initially small in extent in space. When one phase transforms to a more stable phase, the atoms in some region of the first phase must become arranged in the characteristic configuration of the second, if indeed such a characteristic configuration exists. A phase change resulting in *crystal* formation does result in such a characteristic formation. The formation of a crystal in a homogeneous fluid requires that an energy barrier be scaled. The total energy required is the sum of the work to form the particle surface and the work to form the bulk of the particle. The overall excess free energy between a small solid particle of solute and the solute in solution is equal to the sum of the surface excess free energy ΔG_s (i.e., the excess free energy between the surface of the crystal and the bulk of the crystal) and the volume excess free energy ΔG_v (i.e., the excess free energy between the very large crystal and the solute in solution). ΔG_s is positive, its magnitude being proportional to r^2 , where r is the radius of the equivalent spherical solid. In a supersaturated solution, ΔG_v is a negative quantity proportional to r^3 . Thus, the supersaturation is the measurable quantity giving rise to phase change, namely nucleation and crystal growth.

In practice, it is observed that at certain levels of supersaturation, growth will occur but nucleation will not. It is further observed that even at levels of supersaturation which normally support nucleation, nucleation will not occur unless seeds are introduced. These and other observations clearly indicate that

any quantitative examination of crystallization rates must treat nucleation and growth as distinct phenomena. Quite likely, the analytic form of the defining kinetic equation will differ if obtained from phenomenological observations or from theoretical analysis. It is not our purpose here to delve into the details of phase change in crystallization. Ample literature is available on that score. Here, we present a review of some of the concepts and indicate the most probable and useful formulations for studying factors influencing crystal-size distribution. We first consider the most important of the two phenomena, nucleation.

6.1 Nucleation

It has been shown that new crystal formation can result from homogeneous nucleation, heterogeneous nucleation, secondary nucleation, and attrition. Homogeneous nucleation is the formation of new crystals from the liquid phase as a result of the supersaturation alone. Heterogeneous nucleation generally refers to new particle formation resulting from the presence of foreign insoluble material. This foreign material provides sites where crystals can form because of reduced energy requirements. Secondary nucleation refers to nucleation induced by the presence of suspended crystals of the solute. It is to some degree similar to heterogeneous nucleation. It has been called breeding, ancillary nucleation, and other things as well. It is as yet poorly understood. Attrition is simply the mechanical degradation of suspended crystals in which pieces and chips become growing crystals.

All of these phenomena and their effects on size distribution will be discussed in this chapter as well as in Chapter 7.

The fundamental expression for the rate of homogeneous nucleation was proposed as an Arrhenius-type relationship [1]

$$B^0 = c \exp(-\Delta G^*/kT) \quad (6.1-1)$$

where ΔG^* is the free energy of formation of a nucleus, k is Boltzmann's constant, T is the absolute temperature, and c is a proportionality constant. The free energy of formation ΔG^* is the sum of a bulk and a surface contribution. The surface free energy ΔG_s is the product of the surface tension and the surface area of the nucleus. It is difficult to assign a meaningful value to this quantity because of the very small surface area of the nucleus and the virtual impossibility of measuring such quantities. Studies purporting to verify this equation generally involve calculating the surface energy from the experimental nucleation rate data and then making a judgement as to the reasonableness of its magnitude. Most results have been inconclusive.

Using the appropriate relationships connecting geometry, surface tension, free energy, and supersaturation ratio S , Eq. (6.1-1) becomes

$$B^0 = c \exp(-16N\pi M^2 \sigma^3 / 3r^3 T^3 \rho^2 \log^2 S) \quad (6.1-2)$$

where σ is the surface tension, which is usually unknown. The preexponential coefficient c can be shown to be temperature- and supersaturation-dependent and is estimated [2] to be of the order $10^{30} \text{ cm}^{-3} \text{ sec}^{-1}$. This number was estimated in the context of the precipitation of BaSO_4 .

The difficulty with the above expression is that it predicts nucleation only at extremely high supersaturations, a phenomenon not observed in most inorganic crystallization systems. It has been observed, however, in clean systems, where dust and extraneous material have been meticulously removed, that nucleation does not take place even at high supersaturations. In addition to the fact that the equation does not predict rates in a practical sense, it also contains many quantities which are unknown and as yet not determinable.

It has become increasingly evident that homogeneous nucleation is not ordinarily an important phenomenon in industrial crystallizers and, in fact, heterogeneous nucleation or secondary nucleation is generally the most important contributor to new particle formation.

Another nucleation model has been proposed [3] which accounts for heterogeneous effects, namely

$$B^0 = B_n \exp[-(1/kT)(16\pi\sigma^3 v / 3kT \log^2 S)b] \quad (6.1-3)$$

where b is a factor less than one and would account for the fact that σ would be less near a solid-liquid interface. B_n would of necessity be dependent on the number of nucleus sites available for nucleation and hence on the surface area of the nucleating substrata. In the case of secondary nucleation, B_n would depend on the surface area of the solute crystals in suspension. Even with this modified expression, little success has been achieved in predicting experimental behavior.

Nielsen notes that Eq. (6.1-1) can be approximated by a power-law function of supersaturation at a given temperature. However, such approximations require very large power-law exponents. A proposed equation of this power-law form, but which accounts for the observed fact that nucleation does not occur at very low supersaturations, is based on the concept of a metastable region [4] and is given as

$$B^0 = k(C - C_m)^i, \quad C_m > C_s \quad (6.1-4)$$

where C is the solute concentration and C_m is a concentration greater than the

saturation concentration but below which nucleation does not occur. Equation (6.1-4) is referred to as the Miers nucleation model. In most inorganic systems, it appears that C_m is very close to C_s . In experimental work by the present authors, C_m has been taken to equal C_s with considerable success. In such circumstances, Eq. (6.1-4) becomes

$$B^0 = k(C - C_s)^i = ks^i \quad (6.1-5)$$

In Eqs. (6.1-4) and (6.1-5), it is presumed that k can be a function of temperature but that i is not. In a subsequent chapter, we will present some experimental data illustrating the limits of these assumptions.

6.2 Secondary Nucleation

Because of the predominant influence on nucleation rate by a secondary mechanism, it is of interest that we pause here for a further look at this phenomenon. Clontz and McCabe [5], in a unique and informative experimental program, demonstrated that nucleation as a result of contact between crystals in an agitated suspension could well be the most important nucleating phenomenon in industrial crystallization. They found, in various experiments with magnesium sulfate, that high fluid shear near a crystal surface did not induce nucleation but that very low-energy crystal contact gave rise to considerable nucleation. The phenomenon was observed for both crystal-crystal contact and noncrystal-crystal contact, although the former gave rise to the

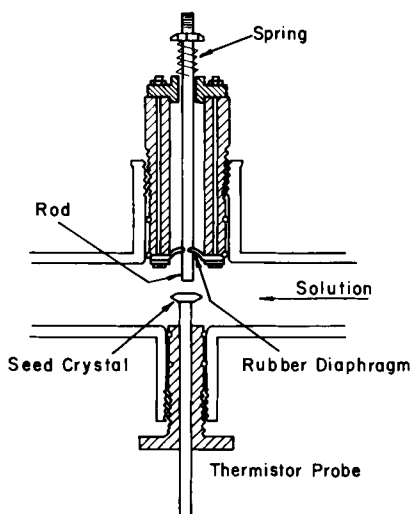


Fig. 6.2-1 Cross section of crystal contacting device [N. A. Clontz and W. L. McCabe, *Chem. Eng. Progr. Symp. Ser. 110* 67 (1971)].

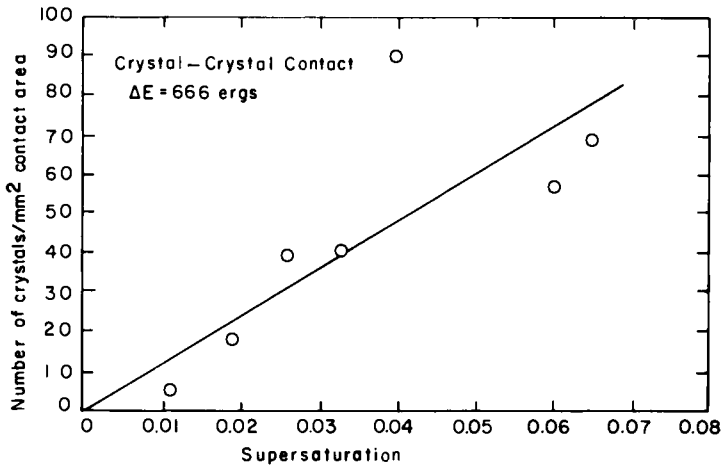


Fig. 6.2-2 Effect of supersaturation on number of particles produced by crystal-crystal contact at contact energy of 666 ergs [N. A. Clontz and W. L. McCabe, *Chem. Eng. Progr. Symp. Ser. 110* **67** (1971)].

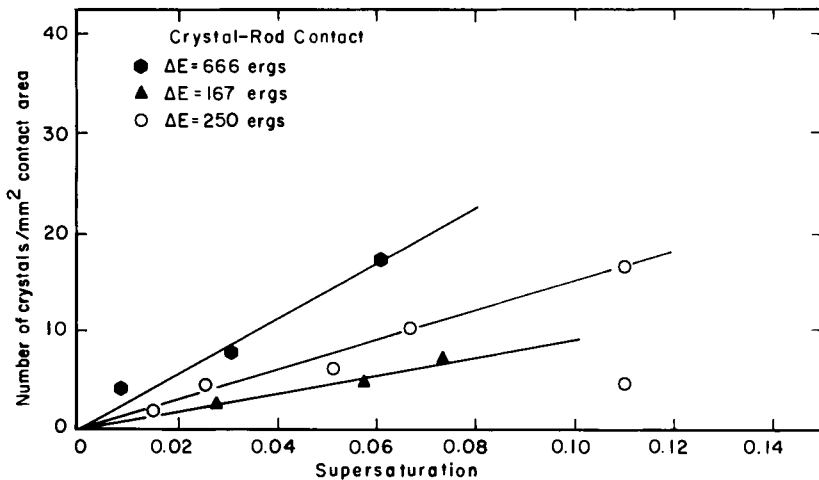


Fig. 6.2-3 Effect of supersaturation on number of particles produced by crystal-rod contact at contact energies of 167, 250, and 666 ergs [A. N. Clontz and W. L. McCabe, *Chem. Eng. Progr. Symp. Ser. 110* **67** (1971)].

greatest number of nuclei. The number produced was also dependent on the supersaturation and on the level of contact energy. They did not observe dendritic growth and fracture under their low-supersaturation experimental conditions.

The apparatus used by Clontz and McCabe is shown diagrammatically in Fig. 6.2-1. In their experiments, a crystal was fixed to an anvil in a long tube through which a supersaturated magnesium sulfate solution was passed. An arrangement was provided directly above the crystal to permit contacting the crystal with a metal rod or another crystal at various levels of contact energy. Downstream from the crystal, a 9-ft growth section was provided. Crystals resulting from contact nucleation collected near the end of this tube and were counted.

Some of the results of this work are shown in Figs. 6.2-2 and 6.2-3. Note that nucleation increases with both contact energy and supersaturation. By comparing the two figures, it is clear that crystal-crystal contact causes more nucleation than does crystal-rod contact. They also found that angular and edge collisions resulted in greater numbers of nuclei than normal surface collisions.

Extending these observations to an agitated suspension, it is clear that impeller-crystal contacts and crystal-crystal impacts should be important contributors to new crystal formation. In heavy magmas, the possible energy of contact levels are lower but the probability of sliding contacts is much greater.

Others [6] have shown in laboratory work that in agitated suspensions, the nucleation rate depends on the number of seeds present, and the authors have demonstrated that nucleation rate is directly related to suspension density.

The results of the work of McCabe and Clontz are consistent with the idea of a fluidized layer near the surface of the crystal which will be dislodged when disturbed by contact. This notion is idealized [7] in Fig. 6.2-4. These experimental results are not, however, consistent with the idea that the layer can be removed by fluid shear. The number of particles dislodged will depend on the size of the crystal, the level of supersaturation, and the energy of contact. The supersaturation level would affect the number produced in two ways. At high supersaturation, the layer would be thicker; hence, there are more particles. In addition, at high supersaturation, the critical size for nucleus survival is smaller; hence, there are more new viable crystals.

In summary, it appears that many secondary and heterogeneous effects can be identified as sources of nuclei. As a consequence, the simple power-law nucleation model [Eq. (6.1-5)] previously given is not adequate as a general representation of nucleation rate. The model must also contain a dependence on the frequency and energy of crystal-crystal contact and agitator-crystal contact. Correlations of these effects are rare, but some work by the authors

Fig. 6.2-4 Power's concept of a fluidized layer near crystal surface. The buffer reservoir layer is dislodged by fluid shear or mechanical penetration to form nuclei. [H. E. C. Powers, *Ind. Chem.* 39, 354 (1963).]



has shown that agitated suspensions undergoing the same energy input exhibit a nucleation power-law dependence on suspension density and supersaturation of the form

$$B^0 = kM_T^j s^i \quad (6.2-1)$$

In many systems, j was found to be unity. Before further refinement can be made, more information must be obtained in order to relate the effects of mechanical energy input to k and j . It should also be pointed out here that the temperature level and the presence of foreign soluble or insoluble material will also effect all quantities and parameters in Eq. (6.2-1).

6.3 Crystal Growth

The mechanism of crystal growth from solution requires that solute be transported to the crystal surface and then oriented into the crystal lattice. Two successive steps are required, a diffusional step followed by a surface reaction step. The latter step is sometimes called the particle integration step and the rate at which the crystal grows because of this mechanism is called the particle integration rate.

If the growth rate is limited by the rate of diffusion through a laminar film, the growth is said to be diffusion-controlled. In many instances, especially in nonagitated systems, this is, in fact, the controlling mechanism. In this case, the mass growth rate may be expressed as follows:

$$dm/dt = (D/X)A(C - C_s) \quad (6.3-1)$$

where D is a diffusion coefficient, X is a film thickness, and A is the surface area of a crystal. $C - C_s$ is the degree of supersaturation and is thought of as the driving force for growth.

It has been observed, however, in some cases, that as agitation increases or as the relative velocity between crystal and mother liquor increases, growth rate reaches a maximum. This is consistent with the concept of diffusion-controlled growth for the low relative solution velocities and with integration (or surface reaction) controlling at high relative velocities.

Several theories have been proposed regarding the nature of the surface growth rate mechanism. Two will be mentioned here. The first is termed nucleation-controlled growth. This mechanism requires that first a "two-dimensional nucleus" be formed on the surface of a growing crystal, followed by growth around the surface discontinuity resulting from the nucleation. The limiting step in this mechanism is the surface nucleation rate, which requires that a rather high energy barrier be surmounted. It is for this reason that this is an improbable growth mechanism for most solutes.

A more probable mechanism is that termed dislocation-controlled growth. By this mechanism, a self-perpetuating dislocation in the crystal lattice causes self-perpetuating surface discontinuities on the crystal, thus providing a supply of low-energy sites for deposit of solute molecules. These dislocations are termed screw dislocations because of the appearance of screwlike surface ridges in photographs of crystals exhibiting this kind of growth.

Small-crystal diffusion-controlled growth and, under some conditions, surface nucleation-controlled growth [8] are related to the growth rate of a characteristic crystal dimension L by

$$G = k(C - C_s)/L = ks/L \quad (6.3-2)$$

For screw-dislocation growth, the rate is given as

$$G = ks^2 \quad (6.3-3)$$

The latter relationship is not often supported experimentally, although data from the K_2SO_4 system [9] indicate growth kinetics described by (6.3-3). Other data on different systems support a linear relationship with supersaturation, however. In fact, most experimental evidence shows an approximate first-order relationship with supersaturation. An equation similar to Eq. (6.3-1) which accounts for both diffusional effects and surface reaction effects has been used with success. Letting k_r be a surface reaction rate constant and assuming linear dependence of the reaction rate on supersaturation gives

$$\frac{dm}{dt} = \frac{DA}{X + (D/k_r)} (C - C_s) \quad (6.3-4)$$

For crystals having size-invariant shape factors k_v and k_a , one may write

$$\frac{k_v \rho}{dt} \frac{d(L^3)}{dt} = \frac{Dk_a L^2}{X + (D/k_r)} s \quad (6.3-5)$$

Then,

$$dL/dt \equiv G = ks \quad (6.3-6)$$

where $k = Dk_a/k_v 3\rho [X + (D/k_r)]$. This is the most useful and applicable growth expression and is used throughout this book. It has one limitation, in that it presumes that growth rate is not a function of crystal size.

It has been observed in several crystallization systems that the growth rate of the characteristic particle size depends on the particle size. Factors causing this size dependence of growth rate (i.e., nonapplicability of McCabe's ΔL law) are poorly understood. For example, it has been observed that $G = G(L)$ for most highly hydrated crystals, although alum is an exception.

This phenomenon is difficult to quantify theoretically but has been handled for analysis purposes by empirical expressions relating the growth rate to crystal size. Various investigators have proposed empirical models intended to account for this described size dependence of growth rate, for size-distribution analysis purposes. Little success has been achieved in relating the variables to a specific theoretical mechanism.

Bransom [10] proposed a power-law model of the form

$$G = ks^a L^b \quad (6.3-7)$$

This relationship can be made to fit data but predicts a zero growth rate as L decreases toward zero, an improbable extension. The authors and their co-workers used a model intended to improve on the limitation of (6.3 7), namely

$$G = G_0(1 + a_1 L) \quad (6.3-8)$$

where G_0 is the growth at zero size and is a function of supersaturation, and a_1 is an empirically determined constant. A further modification utilizes a two-parameter expression given by

$$G = G_0(1 + \gamma L)^b, \quad b < 1 \quad (6.3-9)$$

Again, G_0 is the supersaturation-dependent growth rate at zero size, while b and γ are the two adjustable empirical constants defining the size dependence of the growth rate.

6.4 Summary

We have presented in this chapter a short summary of the theoretical and empirical expressions available for representation of the kinetics of crystallization. In subsequent chapters, we will show how the kinetics affect the size distribution of crystal products. The greatest deficiency in the kinetic information available is the lack of models or data for conditions existing in industrial crystallizers. Data most useful for the analysis of crystallization processes should be taken under conditions when both nucleation and growth occur at measurable rates. For example, the parameters for power-law models can be obtained under such conditions from experiments using the concept of the MSMPR crystallizer and the application of the population balance in the analysis of these data.

Nomenclature

a	Adjustable parameter	L	Crystal size
A	Crystal surface area	m	Mass of crystals
b	Adjustable parameter	M	Mass of crystals
B^0	Nucleation rate	N	Avogadro's number
B_n	Parameter for heterogeneous nucleation	r	Crystal radius
c	Constant	s	Supersaturation as $C - C_s$
C	Solute concentration	S	Supersaturation as C/C_s
D	Diffusion coefficient	t	Time
G	Linear crystal growth rate	T	Temperature
ΔG	Free-energy change	x	Film thickness
i	Order of nucleation (supersaturation)		
j	Order of nucleation (suspension)		
k	Boltzmann constant		
k	Constant		
k_r	Reaction rate constant		
k_v	Volumetric shape factor		

GREEK SYMBOLS

ρ	Density
γ	Adjustable parameter
ρ	Density
σ	Surface tension

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EFFECTS OF FORMATION AND GROWTH KINETICS ON PARTICLE-SIZE DISTRIBUTION

The mechanisms of new particle formation and particle growth are the dominant factors which determine particle size and to some extent the form of the size distribution. It has been shown by experiments that nucleation is in general a nonlinear function of supersaturation, is sometimes a function of the amount of solids in suspension, and is dependent on many mechanical factors of crystallizer design, especially the system geometry and the energy input due to agitation. Generally, increased agitation causes increased new crystal formation. This particle generation is sometimes due to attrition but is more often a result of some secondary nucleation phenomenon. Particle size is affected less by growth than nucleation kinetics, but where size-dependent growth occurs, the form of the distribution is dependent on the growth kinetics.

In this chapter, we will show how the various mechanisms are manifest in observed product size distributions from the continuous, mixed-suspension, mixed-product-removal (MSMPR) crystallizer. In later chapters, we will discuss the effects of unusual residence-time distributions resulting from unusual system geometries.

7.1 Effect of Supersaturation on CSD

The level of supersaturation in an MSMPR crystallizer often markedly affects the CSD of the product. To illustrate the effect of supersaturation on

CSD, we now consider a crystallizer operating at steady state and operable such that suspension density can be fixed at a given level regardless of the holding time. Normally, such a system would be of the Class II type, but the relationships which are developed are applicable for either Class I or Class II systems if the above-mentioned constraint can be applied.

The crystal growth rate is assumed to be a simple function of supersaturation, so that the actual magnitude of the supersaturation can be parametrically excluded from the development:

$$G = G(s) \quad (7.1-1)$$

For nucleation rate which is independent of the effect of suspended solids, we let

$$B^0 = B^0(s) \quad (7.1-2)$$

Eliminating s and assuming a power-law form for the relationship between growth and nucleation gives

$$B^0 = B^0(G) = k_N G^i \quad (7.1-3)$$

Because nucleation rate does not occur explicitly in the expression representing CSD, it is necessary to introduce the relationship

$$B^0 = n^0 G \quad (7.1-4)$$

Combining Eqs. (7.1-3) and (7.1-4) gives

$$n^0 = k_N G^{i-1} \quad (7.1-5)$$

Equation (7.1-5) relates the population density of nuclei to the crystallization kinetics.

It was shown previously for the MSMPR crystallizer, where crystal growth is not size-dependent, that the size distribution given in terms of population density is

$$n = n^0 \exp(-L/G\tau) \quad (7.1-6)$$

Further, it was shown that the suspension density expressed in terms of the distribution is

$$M_T = k_v \rho \int_0^\infty n L^3 dL = 6k_v \rho n^0 (G\tau)^4 \quad (7.1-7)$$

A mass balance relates growth rate to the rate of phase change. Thus,

$$G = \partial C / \left(3k_v \tau \rho \int_0^\infty n L^2 dL \right) = \partial C / 6k_v \tau \rho n^0 (G\tau)^3 \quad (7.1-8)$$

For a system which has only one mixed withdrawal point, $\partial C = M_T$ and (7.1-8) becomes

$$G = M_T / 6k_v \tau \rho n^0 (G\tau)^3 \quad (7.1-9)$$

[Equation (7.1-9) is identical to Eq. (7.1-7).]

In order to compare the effects of supersaturation on CSD, consider two crystallizations carried out at the same temperature but at different supersaturations. A convenient way to assure different supersaturations is to operate at different holding times τ while maintaining the same suspension density. We see from Eq. (7.1-9) that, because of the necessity for conserving mass under such constraints, operation at shorter holding times must produce higher growth rates, hence higher supersaturations.

For crystallizations 1 and 2 operating to produce the same suspension density M_T , we have from Eq. (7.1-7) or (7.1-9)

$$M_T = 6k_v \rho n_1^0 (G_1 \tau_1)^4 = 6k_v \rho n_2^0 (G_2 \tau_2)^4 \quad (7.1-10)$$

or

$$n_2^0 / n_1^0 = (G_1 \tau_1 / G_2 \tau_2)^4 \quad (7.1-11)$$

Using Eq. (7.1-5) to eliminate G_1 and G_2 gives

$$n_2^0 / n_1^0 = (\tau_1 / \tau_2)^{4(i-1)/(i+3)} \quad (7.1-12)$$

and combining Eqs. (7.1-11) and (7.1-5) to eliminate n^0 gives

$$G_2 / G_1 = (\tau_1 / \tau_2)^{4/(i+3)} \quad (7.1-13)$$

Examination of Eqs. (7.1-6), (7.1-12), and (7.1-13) for $\tau_1 > \tau_2$ gives rise to the following observations:

a. When the kinetic order i is equal to one, the size distribution is unaffected by supersaturation level, i.e., $n_1^0 = n_2^0$, $G_1 \tau_1 = G_2 \tau_2$, although growth rates increase in proportion with (τ_1 / τ_2) .

b. When the kinetic order i is greater than one, say three, n^0 increases with a decrease in holding time (increase in supersaturation) by a factor $(\tau_1 / \tau_2)^{4/3}$ and G again increases but to a lesser degree than when $i = 1$, namely by the factor $(\tau_1 / \tau_2)^{2/3}$. The net result is smaller crystal size at shorter holding times (higher supersaturation).

c. When kinetic order is less than one, the crystal size increases with increase in supersaturation.

In summary, it appears that the higher the supersaturation, the smaller the crystal size for systems which exhibit kinetic orders greater than one, and further, the higher the order of nucleation, the more difficult it will be to produce crystals of large size.

EXAMPLE 7.1-1

Two MSMPR crystallizations are carried out at holding times of 15 and 45 min, respectively. The experiments are conducted so that the suspension density M_T is the same for each experiment. The size distributions of the crystalline product are shown in Fig. 7.1-1. Find the order of nucleation for this system.

From Eq. (7.1-12),

$$n_{15}^0/n_{45}^0 = 5 \times 10^7 / 1.15 \times 10^7 = (45/15)^{4(i-1)/(i+3)}$$

For $i = 3$,

$$4.35 = (3)^{4/3}$$

Also from Eq. (7.1-13) and the slopes from Fig. 7.1-1,

$$G_{15}/G_{45} = 1.45/0.70 = (45/15)^{4/(i+3)}$$

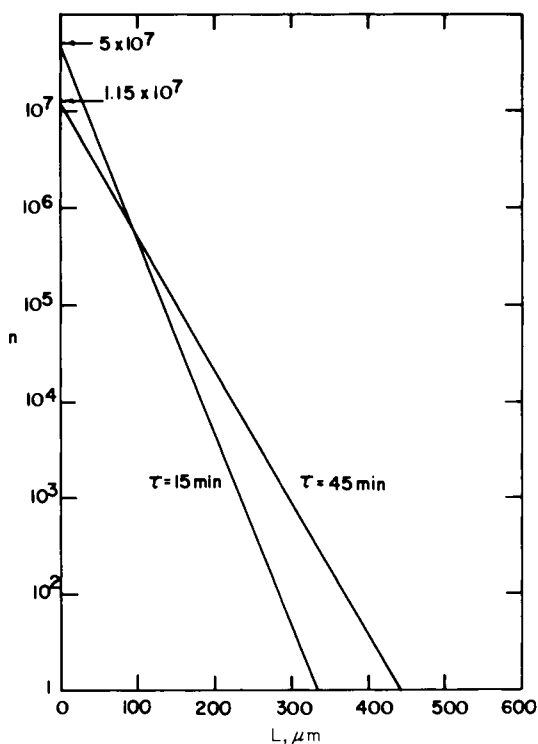


Fig. 7.1-1 Size distribution from crystallization at two different holding times.

For $i = 3$,

$$2.07 = (3)^{2/3}$$

Alternately, the intercepts from Fig. 7.1-1 can be plotted on log-log paper versus the growth rates obtained from the slopes as shown in Fig. 7.1-2. From Eq. (7.1-5), the slope of such a plot is $i-1$. From Fig. 7.1-2, the slope $i-1 = 2$. ♦

If the growth rate is linear with supersaturation, the above example illustrates a useful method for finding i , the nucleation order with respect to supersaturation.

7.2 Effect of Suspended Solids on CSD

Heavy slurry densities provide more surface area for deposition of solute, so that for a given rate of make, lower supersaturations are necessary. This usually results in larger crystals when suspension density is high. In Chapter 8, we will discuss this effect in the context of a growth type crystallizer which has

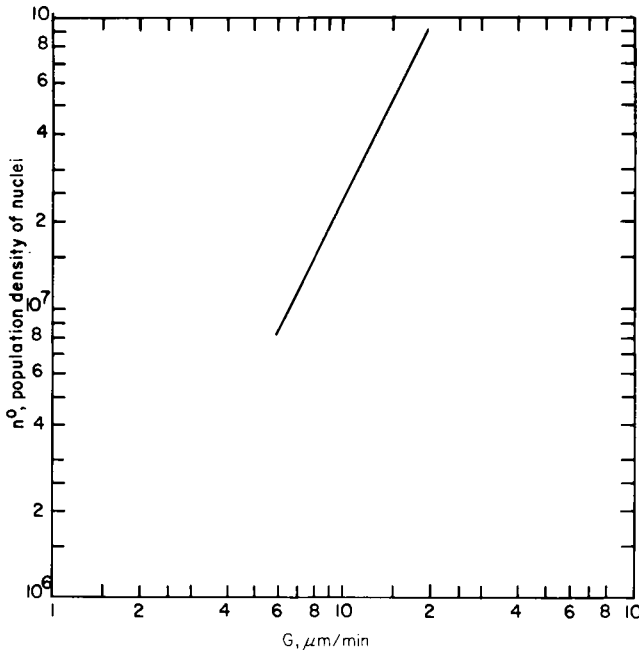


Fig. 7.1-2 Correlation of kinetic order of nucleation i . Slope $i-1 = 2$.

a clear mother liquor withdrawal stream. Here, we will examine the effect of suspension density on CSD for an MSMR crystallizer with only one withdrawal point and for the case where suspended solids are not a source of nuclei. Crystallization systems of this type require an increased rate of make to increase the suspension density.

Consider crystallizations 1 and 2 operated at the same holding time and temperature but with different feed concentration (i.e., $\delta C_1 \neq \delta C_2$). Remembering that $\delta C = M_T$ and $\tau_1 = \tau_2$, from Eq. (7.1-7),

$$\tau^4 = M_{T1}/6k_v \rho n_1^0 G_1^4 = M_{T2}/6k_v \rho n_2^0 G_2^4 \quad (7.2-1)$$

or

$$M_{T1}/n_1^0 G_1^4 = M_{T2}/n_2^0 G_2^4 \quad (7.2-2)$$

Rearranging and using the kinetic relationship (7.1-5), Eq. (7.2-2) becomes

$$G_2/G_1 = (M_{T2}/M_{T1})^{1/(i+3)} \quad (7.2-3)$$

or

$$n_2^0/n_1^0 = (M_{T2}/M_{T1})^{(i-1)/(i+3)} \quad (7.2-4)$$

Finally, the dominant particle size previously given as $L_d = 3G\tau$ is related to the suspension density by

$$L_{d2}/L_{d1} = (M_{T2}/M_{T1})^{1/(i+3)} \quad (7.2-5)$$

The plot shown in Fig. 7.2-1 shows the comparative size distributions where the suspension density (and rate of make) differed by a factor of three. For this example, the kinetic order was two. The nucleation rate, the growth rate, and the dominant particle size are increased with increased suspension density. The distribution curve for the higher suspension density is always above the one for the lower density because the average crystal size is larger and there are more total crystals present. Higher kinetic orders would yield less difference in the observed CSD.

From the above, it is reasonable to expect that for systems where nucleation rate is not of the secondary type, increased suspension density should produce larger crystals.

7.3 Effects of Secondary Nucleation

Most crystallization systems exhibit secondary nucleation effects. When these effects are present, the analysis in Section 7.2 does not apply; therefore, it is necessary to use a kinetic model which accounts for the nuclei formation directly related to the solids in suspension.

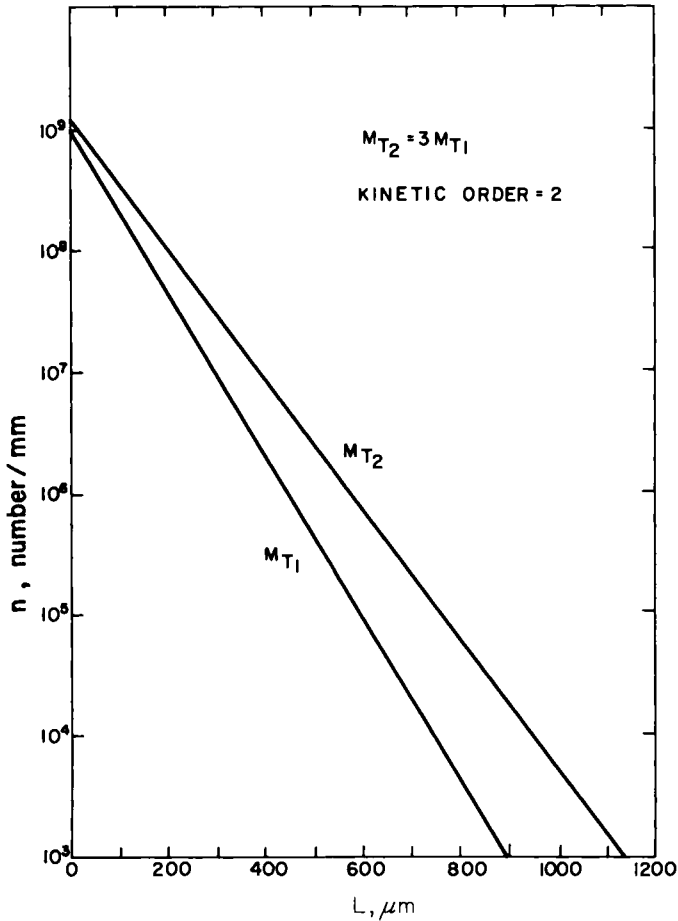


Fig. 7.2-1 Comparison of CSD from crystallizations with different suspension densities (nonsecondary nucleation) [after M. A. Larson, D. C. Timm, and P. R. Wolff, *AIChE J.* 14, 448 (1968)].

Assume that the secondary nucleation rate is related to solids in suspension and supersaturation by

$$B^0 = k M_T^j s^i \quad (7.3-1)$$

where the quantity M_T^j accounts for the secondary nucleation effects. Eliminating supersaturation using a linear form of Eq. (7.1-1) gives

$$B^0 = k_N M_T^j G^i \quad (7.3-2)$$

and in terms of the population density of nuclei,

$$n^0 = k_N M_T^j G^{i-1} \quad (7.3-3)$$

Consideration of a system under the same constraints as that in Section 7.2 operating at two different suspension densities gives

$$M_{T_1}/n_1^0 G_1^4 = M_{T_2}/n_2^0 G_2^4 \quad (7.3-4)$$

Combining this with Eq. (7.3-2) gives

$$n_2^0/n_1^0 = (M_{T_2}/M_{T_1})^{(i+4j-1)/(i+3)} \quad (7.3-5)$$

or

$$G_2/G_1 = (M_{T_2}/M_{T_1})^{(1-j)/(i+3)} \quad (7.3-6)$$

In many instances, the secondary nucleation is found to be proportional to suspension density, and hence $j = 1$. For this case,

$$G_2/G_1 = (M_{T_2}/M_{T_1})^{0.0} = 1 \quad (7.3-7)$$

and

$$n_2^0/n_1^0 = (M_{T_2}/M_{T_1})^{(i+3)/(i+3)} = M_{T_2}/M_{T_1} \quad (7.3-8)$$

From the above equation, growth rate does not change with suspension density and the population density of nuclei changes proportionately with the suspension density (rate of make), regardless of the supersaturation kinetic order i . Consequently, no change in size distribution can be achieved by changing the suspension density of a system with a linear secondary nucleation effect. Size distributions for crystallization with a threefold difference in suspension density are shown in Fig. 7.3-1.

We note here that the same result would occur if secondary nucleation had been assumed to be dependent on crystal area. This analysis cannot distinguish the mechanism of secondary nucleation.

This illustration and that in Section 7.2 indicate only two effects that can be examined via the results of the population balance. It is clear that the rate constant k_N is a function of the hydrodynamic conditions as well as the temperature. In these cases, a more complex analysis and comparison must be made to determine the effect of these conditions and kinetics on size distribution. In subsequent chapters, these factors will be examined in the context of reported experimental data and the effect of residence time will also be examined in the context of systems exhibiting classification.

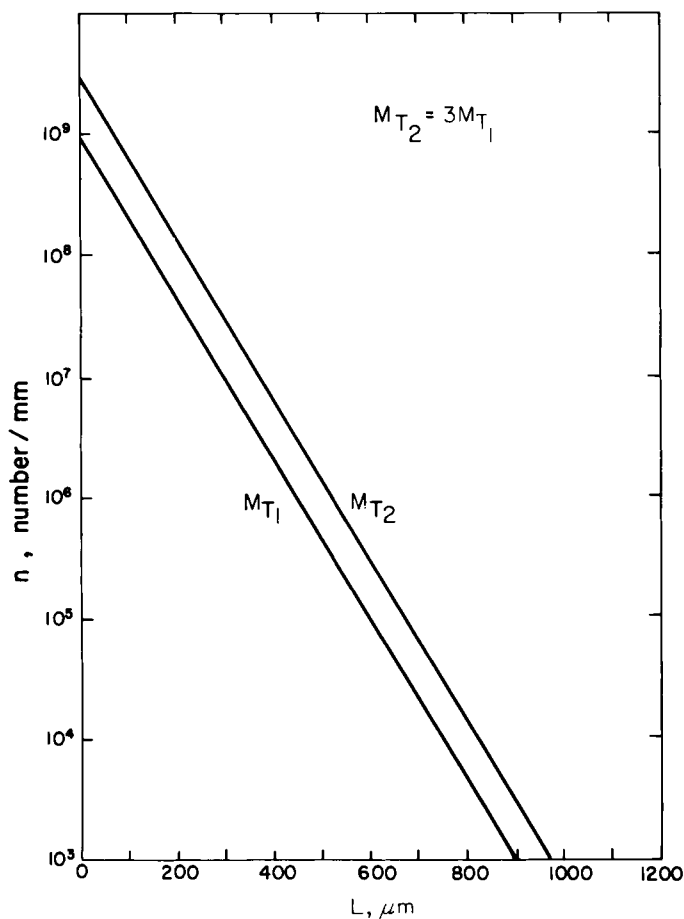


Fig. 7.3-1 Comparison of CSD from crystallization with different suspension densities (secondary nucleation) [after M. A. Larson, D. C. Timm, and P. R. Wolff, *AIChE J.* **14**, 448 (1968)].

7.4 Effects of Size-Dependent Growth Kinetics

Up to this point, the crystal-size distributions from a MSMPR crystallizer have been derived assuming that the growth rate is not an appreciable function of size. In this context, the distribution is the simple exponential

$$n = n^0 \exp(-L/G\tau) \quad (7.4-1)$$

which was obtained by integration of a differential number balance

$$[d(Gn)/dL] + (n/\tau) = 0 \quad (7.4-2)$$

for the case $G \neq G(L)$. However, there is evidence that growth is a function of size in some systems and if an appropriate model for $G(L)$ is available, it can be used in Eq. (7.4-2). A useful two parameter empirical model developed by the authors and their co-workers has been given previously as [Eq. (6.3-9)]

$$G = G_0(1 + \gamma L)^b, \quad b < 1$$

where G_0 , b , and γ are experimentally determined constants, G_0 being the supersaturation-dependent growth rate of a zero-sized crystal, while b and γ are parameters defining the size dependence of the growth rate. The use of (6.3-9) in (7.4-2) gives

$$n(L) = Kn^0(1 + \gamma L)^{-b} \exp[-(1 + \gamma L)^{1-b}/G_0 \tau \gamma (1 - b)] \quad (7.4-3)$$

where $K = \exp[1/G_0 \tau \gamma (1 - b)]$ and where $b < 1$.

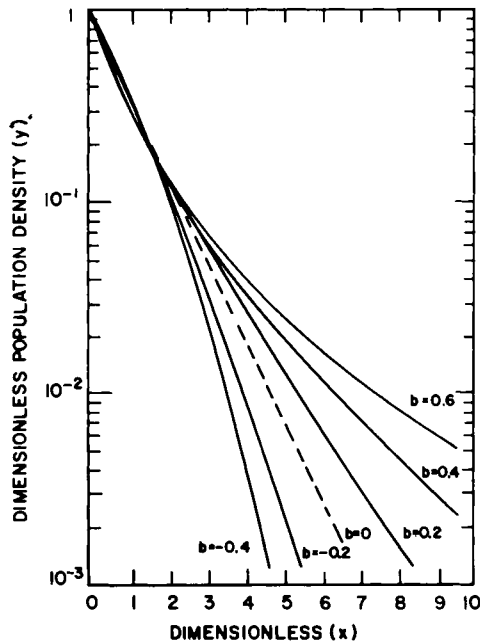


Fig. 7.4-1 Dimensionless CSD from Eq. (7.4-4) [after C. F. Abegg, J. D. Stevens, and M. A. Larson, *AIChE J.* 14, 118 (1968)].

Equation (7.4-3) satisfies all the moment equations previously used, and therefore is quite useful in analyzing systems which exhibit size-dependent growth. It is convenient to cast Eq. (7.4-3) in dimensionless form for analysis of its characteristics. Let $x = L/G_0 \tau$ and $y = n/n^0$, and for $\gamma = 1/G_0 \tau$ [reducing Eq. (6.3-9) to a one-parameter size-dependent equation],

$$y = K(1+x)^{-b} \exp[-(1+x)^{1-b}/(1-b)], \quad b < 1 \quad (7.4-4)$$

Figure 7.4-1 is a plot of this equation for various values of b . When growth rate increases with size, b is positive and one gets semilog plots of the distribution that are concave upward. When growth rate decreases with size, one gets $b < 0$ and distributions which are concave downward.

One must be extremely careful in interpreting experimental data from MSMR crystallizers in light of this equation, however. For example, it is known that the removal of slurry at something other than the isokinetic velocity will cause classification at the discharge. In this event, the residence-time distribution of the crystals is no longer a constant τ , but a function of size $\tau(L)$. Incorporating such a functional relationship in Eq. (7.4-2) will give a result qualitatively indistinguishable from Eq. (7.4-3). This phenomenon will be further discussed in Chapter 8.

7.5 Effect of Crystal Fracture

Well-designed crystallizers agitate and circulate heavy crystal magmas with a minimum of crystal fracture. Heavy slurry densities and long solids retention times inevitably result in crystal attrition, giving rounded crystal habit and increased apparent nucleation rates. Such attrition effects deteriorate particle size but do not materially alter the form of CSD. On the other hand, crystal fracture can significantly shape the particle-size distribution. Crystal fracture represents discontinuous particle trajectories in the particle phase space and is formally represented in the population balance by the birth and death functions B and D . Of course, such terms are meaningless unless they can be described at least empirically in terms of the state of the system. Considerable thought must be taken in formulating these functions to preserve internal consistency; a death event at one size represents two or more birth events at some smaller size(s).

Some generalization and simplification of these birth and death terms is possible, however. Thus, all fractures, no matter how severe, may be approximated by a sequence of two-body death and birth events. If the form of a death function is postulated as a function of the state of the system, a consistent two-body birth function can be constructed to represent the distribution of

resulting pieces. Thus, given a death function $D(L)$, a consistent two-body birth function can be written as

$$B(L) dL = 2 \int_L^\infty P(\xi, L) D(\xi) d\xi dL \quad (7.5-1)$$

where $P(\xi, L) dL$ is the probability that a crystal of size ξ will break into two pieces such that one of the pieces is in the size range L to $L + dL$. Some restrictions can be placed on the probability function $P(\xi, L)$. Normalization requires that

$$\int_0^\xi P(\xi, L) dL = 1 \quad (7.5-2)$$

Further, this probability function P must be symmetric about $\xi/2$ in L space, as breakage events producing a large and a small piece are indistinguishable from events where the size of the two pieces is reversed. This symmetry in L space implies conservation of total length in any breakage event, i.e., $L_1 + L_2 = \xi$, where ξ is the original size breaking down into sizes L_1 and L_2 . In terms of these birth and death functions, conservation of length can be stated as

$$\int_0^\infty D(L) L dL = 2 \int_0^\infty L \int_L^\infty P(\xi, L) D(\xi) d\xi dL \quad (7.5-3)$$

If L remains the characteristic dimension of the particles, with a constant shape factor relating size cubed to particle volume, it is impossible to formulate breakage functions that simultaneously conserve both mass and particle length.

Alternatively, a two body breakage function which conserves mass rather than length can be formulated. Let $P_m(\xi, L^3) d(L^3)$ be the probability that one of the pieces from a two body breakage event at size ξ breaks into a piece of size L^3 to $L^3 + d(L^3)$. Again, normalization requires that

$$\int_0^\xi P_m(\xi, L^3) d(L^3) = 1 \quad (7.5-4)$$

and symmetry requires that P_m be symmetric about $\xi^3/2$ on a plot of P_m versus L^3 in the interval $(0, \xi^3)$. In terms of these breakage functions, conservation of mass is given as

$$\int_0^\infty D(L) L^3 dL = 2 \int_0^\infty L^3 \int_L^\infty P_m(\xi, L^3) D(\xi) d\xi d(L^3) \quad (7.5-5)$$

A consistency check on two-body breakage functions is that the total number of pieces formed is twice the number broken. In terms of the B and D , functions this restriction becomes

$$2 \int_0^\infty D(L) dL = 2 \int_0^\infty \int_L^\infty P(\xi, L) D(\xi) d\xi dL \quad (7.5-6a)$$

or

$$2 \int_0^\infty D(L) dL = 6 \int_0^\infty L^2 \int_L^\infty P_m(\xi, L^3) D(\xi) d\xi dL \quad (7.5-6b)$$

These breakage terms can be further generalized in terms of a dimensionless probability coordinate ε defined as

$$\varepsilon = L/\xi \quad (7.5-7)$$

where ε is in the normalized interval (0, 1). Under this transformation, these two-body birth functions become

$$B(L) = 2L \int_0^1 [P(\varepsilon, \xi) D(L/\varepsilon) d\varepsilon/\varepsilon^2] \quad (7.5-8a)$$

or

$$B(L) = 6L^3 \int_0^1 [P_m(\varepsilon^3, \xi) D(L/\varepsilon) d\varepsilon/\varepsilon^2] \quad (7.5-8b)$$

Three idealized probability distributions are shown in Fig. 7.5-1 for the case where the probability distribution is independent of the size at which breakage occurred, i.e., $P(\varepsilon, \xi) = P(\varepsilon)$. Figure 7.5-1(a) describes the situation where there is a uniform chance that the broken pieces will be any size less than ξ . Figure 7.5-1(b) describes the situation where breakage results in essentially two pieces of equal size. In the limit as the peak shown becomes a spike at $\varepsilon = 0.5$, no integration over the probability coordinate is necessary and the birth function can be written simply as

$$B(L) = 2D(2L) \quad (7.5-9a)$$

or if mass is conserved,

$$B(L^3) = 2D(2L^3) \quad (7.5-9b)$$

Breakage in equal pieces produces the maximum effect in altering the form of CSD. Figure 7.5-1(c) describes the situation where a very small fragment is broken off from the original particle at size ξ . In the limit, this represents crystal attrition. The net effects are an apparent increase in nucleation, an apparent decrease in growth rate with possible rounding of larger crystals, and no major change in the form of CSD.

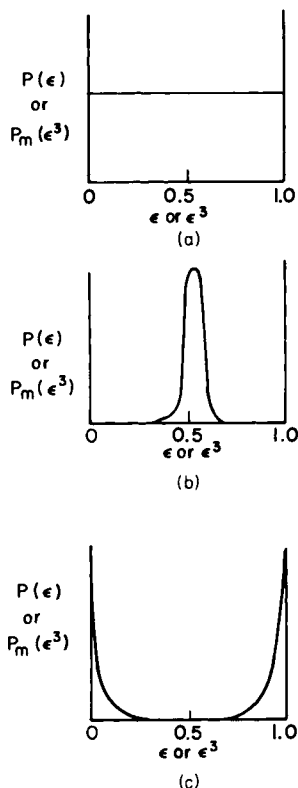


Fig. 7.5-1 Idealized probability distributions for crystal breakage. (a) Uniform, (b) equal-size, (c) attrition breakage distributions. [Reprinted from *Ind. Eng. Chem. Fundamentals* 8, 58 (1969). Copyright 1969, American Chemical Society, reprinted by permission of the copyright owner.]

EXAMPLE 7.5-1

Predict the effect of crystal breakage on the form of CSD in a Class II MSMPR crystallizer and compare this to the theoretical MSMPR CSD. Assume a two-body, equal-sized, length-conserving birth function as shown by $P(\epsilon)$ in Fig. 7.5-1(b). Assume that breakage at size L is proportional to the population at that size times a power-model weighting factor. Thus,

$$D(L) = knL^\beta \quad (7.5-10)$$

$$B(L) = 2^{\beta+1} kn(2L)L^\beta \quad (7.5-11)$$

where k and β are constants representing breakage rate and size selectivity, respectively. The population balance for the MSMPR crystallizer with breakage is given as

$$G(dn/dL) + (n/\tau) = 2^{\beta+1} kn(2L)L^\beta - knL^\beta \quad (7.5-12)$$

where $\tau = V/Q$ is the retention time in the MSMPR crystallizer. Substituting the dimensionless variables $x = L/G\tau$, $y = n/n^0$, and $K = k(G\tau)^{\beta+1}\tau$ yields

$$(dy/dx) + (1 + Kx^\beta)y = 2^{\beta+1}Kx^\beta y(2x) \quad (7.5-13)$$

with boundary condition $y(0) = 1$.

The effect of crystal fracture on the form of CSD from an MSMPR crystallizer can be studied by solving Eq. (7.5-13) for various values of the dimensionless breakage constant K . For purposes of illustration, we fix the breakage constant K in terms of the ratio of particles broken at the MSMPR dominant size ($x = 3$) to those removed in the mixed product at this size. Letting this ratio be m , we obtain

$$m = Kx^\beta y/(1)y|_{x=3} \quad (7.5-14)$$

or $K = m/3^\beta$, and the population balance becomes

$$(dy/dx) + [1 + m(x/3)^\beta]y = 2^{\beta+1}m(x/3)^\beta y(2x) \quad (7.5-15)$$

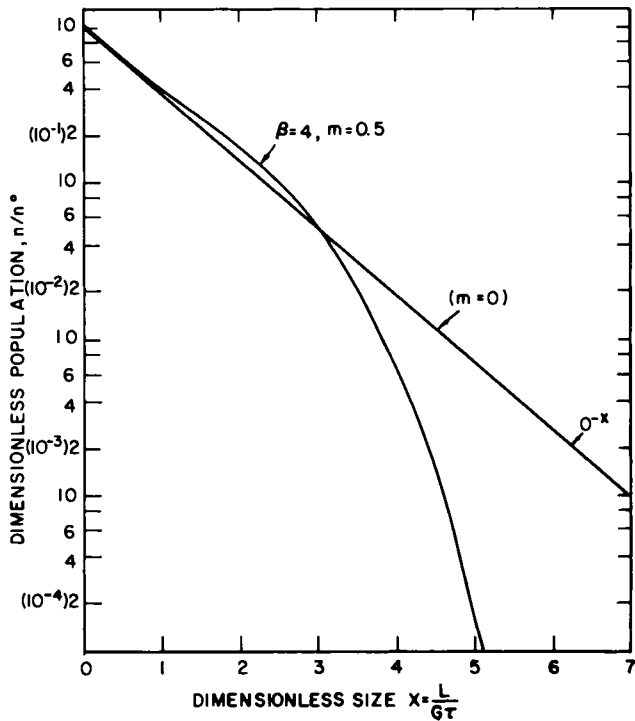


Fig. 7.5-2 Effect of crystal breakage on population density in a mixed suspension crystallizer. [Reprinted from *Ind. Eng. Chem. Fundamentals* 8, 58 (1969). Copyright 1969, American Chemical Society, reprinted by permission of the copyright owner.]

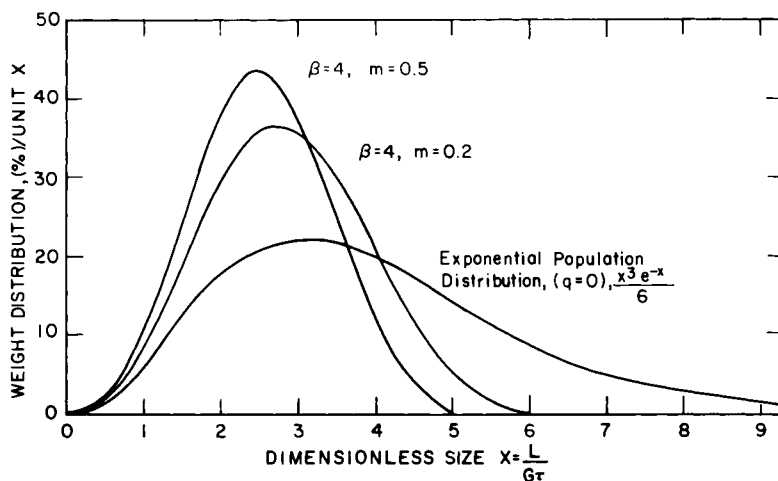


Fig. 7.5-3 Effect of crystal breakage on CDS in a mixed suspension crystallizer. [Reprinted from *Ind. Eng. Chem. Fundamentals* 8, 58 (1969). Copyright 1969, American Chemical Society, reprinted by permission of the copyright owner.]

where m represents the fraction of breakage relative to removal at the MSMPR dominant size. Equation (7.5-15) was solved for various values of m and β and compared with the ideal MSMPR CSD. Constant density of nuclei was assumed in these calculations. In practice, increases in crystal area brought about by crystal breakage would result in a lowering in driving forces, giving different densities of nuclei. A more realistic simulation of breakage effects could be obtained by including power-law nucleation-growth rate kinetics and a mass-balance growth-rate constraint together with Eq. (7.5-15) as a complete statement of the problem.

The effect of breakage on the form of CSD is illustrated for the above-described case. Figure 7.5-2 is a population density plot for the case where breakage is severely size-dependent ($\beta = 4$) with breakage equal to 50% of the mixed removal rate at a dimensionless size of $x = 3$. Population density decays severely for large particle sizes, much as in the case of classified product removal, thus producing a narrower CSD of smaller average size. Figure 7.5-3 illustrates this narrowing effect by plotting the predicted weight distribution curves for 0, 20, 50% breakage (relative to mixed discharge) at the dominant size.

The form of the breakage function used in this example, Eq. (7.5-9a), conserves length rather than mass and hence the calculated solids concentration changes with the degree of breakage. This computational artifact resulting from the assumed birth function was of no consequence in this case; when a complete simulation using nucleation-growth rate kinetics is attempted, the mass-conserving form of the birth function should be chosen. ♦

VARIATIONS IN RESIDENCE-TIME DISTRIBUTIONS

8.1 Introduction

The study of CSD in crystallizers of complex process configuration is in essence a study of the mean retention probabilities of individual particles as a function of their size and, hence, age. For well-mixed systems with size-independent growth rates, the form of CSD is completely specified by the residence-time distribution in the process. Indeed, the size of each individual particle is related to its age in the system as

$$L = G\tau \quad (8.1-1)$$

Thus, the form of CSD is completely specified by the residence-time distribution. Although the form of the distribution is specified by the residence-time distribution, the particle size is largely determined by the solute resources available (mass balance) and the relative kinetics of growth and nucleation. Variations in residence time of solids versus liquid and of solids versus solids, as functions of particle size affect CSD and both must be considered in process modeling. Figure 8.1-1 illustrates the interrelationships of factors affecting CSD.

A general CSD algorithm for a backmixed stage of volume V can be developed which can account for completely arbitrary residence-time distributions. Consider the most general case of a backmixed, steady-state crystal

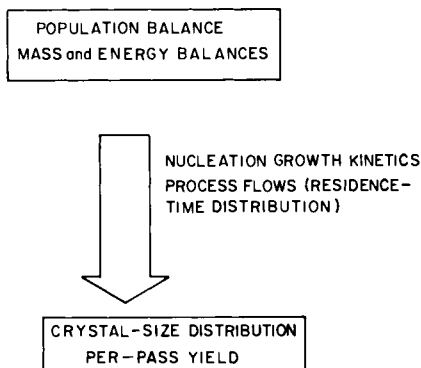


Fig. 8.1-1 General algorithm for calculation of crystal-size distribution.

magma (Fig. 8.1-2) having j slurry inputs of flow rate $Q_{i,j}$ with population density $n_{i,j}$ and k slurry outputs with flow $Q_{o,k}$ and population density $n_{o,k}$. The steady-state macroscopic population balance for this case, assuming negligible crystal fracture, reduces to

$$V \frac{d}{dL} (Gn) = \sum_j Q_{i,j} n_{i,j} - \sum_k Q_{o,k} n_{o,k} \quad (8.1-2)$$

Equation (8.1-2) can be reduced to a nonhomogeneous, variable-coefficient equation of fixed form whose solution generates CSD for completely arbitrary process configurations, depending only upon the form of the nonhomogeneous, nonconstant-coefficient terms. These terms are composed after consideration of the particular process configuration to be simulated, and input into the population balance used as a general CSD algorithm. Development of this

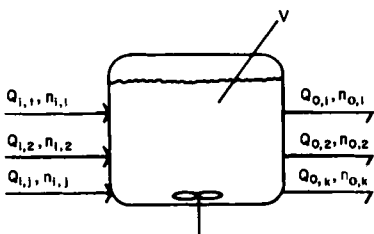


Fig. 8.1-2 Generalized model of a mixed magma crystallizer with arbitrary process configuration.

idea proceeds as follows. Choose a reference flow Q_B . It is normally chosen as net liquor flow. Define a bucket-mixing average for inlet slurries as

$$Q_i n_i = \sum_j Q_{i,j} n_{i,j}, \quad \text{where} \quad Q_i = \sum_j Q_{i,j} \quad (8.1-3)$$

Further, define each outlet stream as being proportional to the distribution n . Thus, $Q_{o,k}n_{o,k} = Q_{o,k}(L)n$, where $Q_{o,k}(L)$ is the equivalent mixed-suspension removal rate at size L , giving

$$\sum_k Q_{o,k}n_{o,k} = \sum_k Q_{o,k}(L)n \quad (8.1-4)$$

Define total removal at size L as $\sum_k Q_{o,k}(L) = Q_o(L)$. Further, define a withdrawal function $C_w(L)$ as $C_w(L) = Q_o(L)/Q_B$. Thus, the total output term is given as

$$\sum_k Q_{o,k}n_{o,k} = Q_B C_w n \quad (8.1-5)$$

Substitution in the population balance gives

$$V \frac{d}{dL} (Gn) = Q_i n_i - Q_B C_w n \quad (8.1-6)$$

Assume that growth rate is some function of L . Define $g(L) = G(L)/G_o$, where G_o is some reference growth rate, usually the average growth rate, in some sense, or the zero-sized particle growth rate. Making the substitution gives

$$G_o V [d(gn)/dL] = Q_i n_i - Q_B C_w n \quad (8.1-7)$$

as the generalized population balance for the backmixed volume V . Let $y = gn/n_o^0$, giving $n = yn_o^0/g$. Then,

$$n_o^0 G_o V (dy/dL) = Q_i n_i - (Q_B C_w n_o^0 y/g) \quad (8.1-8)$$

Let a dimensionless x be given as $x = LQ_B/VG_o$. Making this substitution gives

$$dy/dx = (Q_i n_i/n_o^0 Q_B) - [C_w(x)/g(x)] y \quad (8.1-9)$$

Further, let $Q_i/Q_B = \alpha$ and $y_i = g(0)n_i/n_o^0$. Then,

$$dy/dx + [C_w(x)/g(x)] y = \alpha y_i(x)/g(0) \quad (8.1-10)$$

If $G_o = G(0)$, then $g(0) = 1$ and a boundary condition for solution of this equation becomes $y(0) = 1$. Equation (8.1-10) is a dimensionless, variable-

coefficient, nonhomogeneous differential equation which is constant in form and serves as a central algorithm for CSD computations; it is dependent in its solution on the form of the size-dependent inputs $g(x)$, $y_i(x)$, and $C_w(x)$.

The crystallizer is assumed to be at steady state and therefore at constant production rate, even if it does not represent 100% yield. This production will also be a function of how much mass is fed into the vessel as seed, if the crystallizer is seeded. Writing the production in terms of exit slurry flows gives

$$P = \sum_k Q_{o,k}^p M_{o,k} \quad (8.1-11)$$

where $Q_{o,k}^p$ is that outlet stream going to product and $M_{o,k}$ is the solids concentration in the stream. (Note: There is an essential difference between the cases of fines dissolution and split underflow/overflow discharge; not all of the withdrawn streams in the former case go to the product stream. Clearly, $\sum_k Q_{o,k}^p M_{o,k} \leq \sum_k Q_{o,k} M_{o,k}$.) Solids concentration is given in terms of population density as

$$M_T = \rho k_v \int_0^\infty n L^3 dL \quad (8.1-12)$$

Production is thus given in terms of population density and withdrawal flow to product as

$$P = \rho k_v \int_0^\infty Q_o^p(L) n L^3 dL \quad (8.1-13)$$

Defining $C_p = Q_o^p(L)/Q_B$, then

$$P = Q_B \rho k_v \int_0^\infty C_p n L^3 dL \quad (8.1-14)$$

where clearly $C_w \geq C_p$. Equations (8.1-10) and (8.1-14) are solved, together with appropriate nucleation-growth rate kinetics, to define population densities in the system.

Finally, CSD's on a weight basis, in the suspension and product, are calculated from the population distribution as

$$W(L) = \int_0^L n L^3 dL / \int_0^\infty n L^3 dL \quad (8.1-15)$$

and

$$W_p(L) = \int_0^L C_p(L) n L^3 dL / \int_0^\infty C_p(L) n L^3 dL \quad (8.1-16)$$

EXAMPLE 8.1-1 USE OF GENERALIZED BACKMIXED MODEL

Briefly explain how this generalized CSD algorithm would be used to simulate the cases of staging (or seeding), size-dependent growth rate, classified product removal, and fines dissolving.

A. Staging (Seeding)

Staging is a special case of seeding wherein all but the first vessel are seeded by the discharge from previous stages. This is handled, say for the k th stage, by allowing

$$\alpha y_i = (Q_B C_w n)_{k-1} / (Q_B n_0)_k \quad (8.1-17)$$

which can be programmed in a sequence of applications of the central backmixed algorithm. If seeding is achieved through addition of a truly external source, say from another system, then the function αy_i can be constructed from the cumulative CSD, solids concentration, and source of the external slurry stream from the preceding development and the definition

$$n_i = (M_{Ti}) (dW_i/dL) / \rho k_v L^3 \quad (8.1-18)$$

B. Size-Dependent Growth Rate

If the coefficient $g(x)$ in Eq. (8.1-10) varies with x , this simulates size-dependent growth rate. The most convenient normalization of the size-dependent growth rate would be division by the nucleus growth rate $G(0)$, thus preserving the unity boundary condition for Eq. (8.1-10). The function $g(x) = 1$ for all x is tantamount to McCabe's ΔL law. If the function $g(x)$ increases with x , the distribution is wider than the MSMR case; if $g(x)$ decreases with x , a narrower distribution is produced. Changes in growth rate with size are similar, but not identical, to changes in mean retention probability as a function of size, given as $\tau(x) = V/Q_o(x)$ and represented by the $C_w(x)$ function.

C. Classified Product Removal

In this mode of operation, separations of residence-time probability as a function of size, $C_p(x) = V/Q_o(x)$, is accomplished by size-segregation devices, e.g., wet screens, hydroclones, elutriators, etc. For this case, the classification occurs in the product stream and $Q_o(x) = Q_o^p(x)$. Such classification is handled by the $C_w(x) = C_p(x)$ functions, which physically can be interpreted as the ratio of actual removal at size L to the removal rate expected with mixed withdrawal.

A highly idealized representation of product classification useful for simulation of wet screens and hydroclones is

$$Q_o(L) = Q_o \quad \text{for } L < L_p$$

$$Q_o(L) = zQ_o \quad \text{for } L > L_p$$

or equivalently,

$$C_w = C_p = 1 \quad \text{for } x < x_p$$

$$C_w = C_p = z \quad \text{for } x > x_p$$

where z is the feed-to-product ratio of the classifying device, L_p is the size cut point, and Q_o is the mother-liquor flow rate carried with the product.

D. Fines Removal

The effect of fines removal is simulated by the function $C_w(x)$. In this case, fine particles less than some small size, say L_F , are removed at an accelerated rate. Thus, to simulate this process modification, let

$$C_w > 1 \quad \text{for } x < x_F$$

$$C_w = 1 \quad \text{for } x > x_F$$

For this case, $C_p = 1$ for all sizes as the fines are dissolved, not sent to product. (Note: As far as the distribution which develops in the mixed suspension is concerned, it matters little whether the fines are dissolved and recycled, sent to product, or dumped on the floor, although growth rate will be somewhat higher in the former case.) ♦

All of the above four process configurations and any combination of them can be rigorously simulated by empirical specification of the four functions of size, namely, $y_1(x)$, $g(x)$, $C_p(x)$, and $C_w(x)$, together with numerical solution of Eqs. (8.1-10) and (8.1-14), and with an empirical expression for secondary nucleation kinetics. CSD expressed on a weight basis is then calculated, in suspension and product, from Eqs. (8.1-15) and (8.1-16).

8.2 Growth-Type Crystallizer

In commercial crystallizer designs, residence times of mother liquor and solids are often separated to provide better yield and size improvement. In such a design, the so-called "growth-type" crystallizer, a clear liquor advance is provided from a quiescent settling zone (external or internal to the main crystallizer body), allowing removal of a heavier slurry at a lower rate in a mixed-suspension underflow stream. Such operation results in higher yields from Class I systems and, depending upon the form of secondary nucleation kinetics, can improve or degenerate particle size.

Such a process configuration can easily be analyzed if the idealization that particles are completely removed from the clarified stream is made, as the MSMPR form of the distribution remains unaltered. If the carry-over size of particles in the clarified overflow stream is known, the process can be analyzed by the more rigorous treatment described in Section 8.1.

Consider the idealized case where a perfectly clear mother liquor Q_o is assumed to be removed in the settled overflow stream. Mixed discharge occurs in the underflow stream Q_u , and thus CSD is given by the MSMPR relation as

$$n = n^0 \exp(-LQ_u/GV) \quad (8.2-1)$$

Further, assume nucleation-growth rate kinetics are given as

$$n^0 = k_N G^{i-1} \quad (8.2-2)$$

which at this point neglects any explicit CSD dependence of secondary nucleation. This is a very restrictive assumption and will be relaxed later. Assuming high yield (Class II system), production rate is independent of the amount of clear liquor overflow. Thus, comparing crystallizers under the above assumptions with or without clear liquor overflow, referred to with subscripts 2 and 1, respectively, gives

$$P_1 = P_2$$

or

$$Q_{u1} \rho k_v \int_0^\infty n_1 L^3 dL = Q_{u2} \rho k_v \int_0^\infty n_2 L^3 dL \quad (8.2-3)$$

Performing the indicated integrations and canceling yields

$$Q_{u1} (G_1 \tau_1)^4 n_1^0 = Q_{u2} (G_2 \tau_2)^4 n_2^0 \quad (8.2-4)$$

Substituting kinetics gives

$$Q_{u1} (G_1 \tau_1)^4 G_1^{i-1} = Q_{u2} (G_2 \tau_2)^4 G_2^{i-1} \quad (8.2-5)$$

Multiplying and dividing each side by $(V/Q_u)^{i-1}$ and recognizing that $3G\tau = L_d$ is the dominant size in the distribution gives

$$L_{d2}/L_{d1} = (Q_{u1}/Q_{u2})^{i/(i+3)} \quad (8.2-6)$$

Thus, as the flow ratio $Q_{u1}/Q_{u2} = (Q_u + Q_o)/Q_u > 1$, then, as Q_u is reduced due to clear liquor overflow Q_o , some size improvement is expected in a

growth-type crystallizer. If nucleation rate is not a function of the driving forces in the system, $i \leq 0$ no increase, or perhaps a decrease, in particle size would be expected.

As mentioned previously, the assumption that secondary nucleation did not depend explicitly on CSD was of dubious validity. More reasonable secondary nucleation kinetics include the effect of solids concentration, as in the general power-model form

$$n^0 = k_N G^{i-1} M_T^j \quad (8.2-7)$$

Repeating the previous derivation with the above kinetics gives a more realistic appraisal of expected size improvement. Again, production rate, with or without clear liquor overflow, is a constant. Thus,

$$Q_{u1} M_{T1} = Q_{u2} M_{T2} \quad (8.2-8)$$

But from the definition of solids concentration and power-law kinetics of the form Eq. (8.2-7) one obtains

$$M_T^{1-j} = 6\rho k_v k_N (G\tau)^{i+3} Q_u^{i-1} / V^{i-1} \quad (8.2-9)$$

Or, substituting,

$$Q_{u1} [Q_{u1}^{i-1} (G_1 \tau_1)^{i+3}]^{1/(1-j)} = Q_{u2} [Q_{u2}^{i-1} (G_2 \tau_2)^{i+3}]^{1/(1-j)} \quad (8.2-10)$$

Again, recognizing that the dominant size is proportional to the growth rate times retention time gives

$$L_{d2}/L_{d1} = (Q_{u1}/Q_{u2})^{(i-j)/(i+3)} = \left(\frac{Q_u + Q_o}{Q_u} \right)^{(i-j)/(i+3)} \quad (8.2-11)$$

Note that when $j = 0$, Eq. (8.2-11) reduces to the special case of Eq. (8.2-6). When the nucleation power-law exponents on growth rate and solids concentration are equal, no size improvement occurs. When the exponent on solids concentration exceeds that on growth rate particle size actually decreases. As an example, for typical values of the power-law exponents, say $i = 2$ and $j = 1$, the size improvement ratio would vary with the $\frac{1}{3}$ power of the total flow/underflow ratio, indicating relatively small size improvement.

In fact, growth-type crystallizers often improve particle size more effectively than suggested by Eq. (8.2-11). This is undoubtedly due to the significant decay of population which occurs due to the so-called "clear" overflow stream. Thus, in any real classification system, the overflow stream acts as a low-capacity fines-removal system, increasing particle size. Such a process could be rigorously analyzed by the methods of Section 8.1.

8.3 Fines Destruction

Relative nucleation–growth rate kinetics of many crystal systems are such that under ordinary process conditions in an MSMR crystallizer, the particles are of less than desired average size. Increases in the mean retention time, besides increasing capital investment and/or decreasing production throughput, are not very effective in bringing about an increase in particle size. The predicted variation in dominant particle size derived analogously to Eq. (8.2-11), using the realistic secondary nucleation kinetics of Eq. (8.2-7), for a Class II MSMR crystallizer is

$$L_{d2}/L_{d1} = (\tau_2/\tau_1)^{(i-1)/(i+3)} \quad (8.3-1)$$

Note that for a Class II system, solids concentration is independent of retention time and the exponent j does not appear in Eq. (8.3-1). As values of i for low-order secondary nucleation kinetics might typically be in the range 0–3, it is obvious that little size improvement, and perhaps even size degeneration, will be brought about by increases in total retention time.

A more practical way of increasing particle size is by preferential removal of the smaller sizes, leaving the remaining crystals to grow to larger average size. If fines can be removed at a small enough size, it is immaterial to size improvement whether they are advanced to product or dissolved and recycled; however, the removal of large flows of liquor associated with the fines dictates that they be dissolved and the liquor recycled. The net effect of fines destruction is to force the growth rate to higher levels, producing the same production on fewer crystals of larger average size.

The potential and limitations of size improvement with fines destruction can be easily developed using the concept of a point fines trap, i.e., fines removal at a size negligibly small compared to product-size crystals. For this case, both solids concentration (for Class II system) and the mean retention time of the surviving crystals remain invariant when fines destruction is implemented, thus the growth rates, and hence dominant particle sizes, are inversely proportional to specific crystal surface area. The ratio of size improvement with the destruction of nuclei is then given as

$$L_{d2}/L_{d1} = \int_0^\infty n_1 L^2 dL / \int_0^\infty n_2 L^2 dL = n_1^0 (L_{d1})^3 / \beta n_2^0 (L_{d2})^3 \quad (8.3-2)$$

where β is the fraction of nuclei surviving the fines-destruction system and where the subscripts 2 and 1 refer to the cases with and without fines destruction, respectively. Assuming the power-law form of kinetics of Eq. (8.2-7),

gives

$$(L_{d_2}/L_{d_1})^4 = (G_1/G_2)^{i-1}/\beta \quad (8.3-3)$$

Multiplying top and bottom by τ^{i-1} and solving for the size improvement ratio gives

$$L_{d_2}/L_{d_1} = (1/\beta)^{1/i+3} \quad (8.3-4)$$

Thus, because of the increased nucleation caused by higher driving forces, the effectiveness of fines destruction in increasing particle size decreases with systems having a high sensitivity of nucleation to growth rate, indicated by large values of the parameter i . From this equation, one could deduce that a fines-removal system would be quite ineffective in increasing particle size beyond a level where the increased driving forces pushed nucleation past a metastable limit. The maximum size improvement occurs with the lowest nucleation-growth rate sensitivity measured by the parameter i . Values of β as small as 10^{-3} , i.e., only one nuclei in one thousand surviving the fines-destruction system, can occur in commercial units, and thus fines destruction within the metastable range of operation is an effective means of size improvement.

The effect of fines destruction when the fines are not negligibly small compared to product-size crystals and represent an appreciable solute recycle stream, thus increasing the internal rate of make and altering the form of CSD, can be rigorously analyzed by the techniques in Section 8.1. In terms of the general algorithm, fines destruction is simulated by allowing the removal function $C_w(L)$ to be much greater than unity for sizes less than the maximum fines size, L_F , and equal to unity for sizes larger than L_F . Assuming the fines are dissolved and recycled, the product removal function $C_p(L)$ is unity for all sizes. If fines are advanced to product rather than dissolved, $C_p(L) = C_w(L)$ for all L . Physically, the $C_w(L)$ function represents the ratio of the combined fines and mixed-product flow rates to the mixed-product rate.

Accelerated removal of fines often produces a bimodal weight distribution in the product crystals: a small peak within the size range $(0, L_F)$ and the normal mode at the dominant crystal size. Such a bimodal mass distribution will occur any time smaller crystals have an appreciably shorter mean retention probability than larger crystals, such as in a growth-type crystallizer with a partially clarified overflow stream. The condition for producing a mass peak in a small size range $(0, L_F)$, and hence a bimodal distribution, is

$$3GV/(Q_F + Q_m) < L_F \quad (8.3-5)$$

where Q_F is the fines-removal rate (or overflow rate for growth-type unit) and Q_m is the mixed-product underflow rate. Normally, a bimodal distribution

is of no consequence, but if the first peak represents too large a fraction of the distribution, the product may become difficult to filter or dusty in appearance.

EXAMPLE 8.3-1

Using the previously derived theory, construct a hypothetical semilog population density plot of CSD from a crystallizer before and after the addition of a fines-removal system, considered as cases 1 and 2, respectively. For this example, in case 2, it is assumed that fines, in sizes 0 to L_F , are withdrawn with a flow rate $(R-1)Q_o$, while product crystals, in the size range L_F to ∞ , are withdrawn at a rate Q_o , and where R is the ratio of product-to-fines drawdown times. Thus, the drawdown times will be

$$\begin{aligned}\tau_F &= V/RQ_o & \text{for } L < L_F \\ \tau_p &= V/Q_o & \text{for } L > L_F\end{aligned}$$

From previous theory it is known that crystal population in each size range will decay exponentially, inversely proportional to the product of growth rate times holding time. Thus, the population densities will be of the form

$$\begin{aligned}(n_F)_2 &= C_1 \exp(-L/G_2 \tau_F) & \text{for } L < L_F \\ (n_p)_2 &= C_2 \exp(-L/G_2 \tau_p) & \text{for } L > L_F\end{aligned}\tag{8.3-6}$$

where C_1 and C_2 are constants. Furthermore, $n_F = n_p$ when $L = L_F$, as the distribution is surely continuous. Thus, on the semilog plot (Fig. 8.3-1), a straight line can be drawn in the segment 0 to L_F with a negative slope R times that in the range (L_F, ∞) of the product crystals. The curve for the mixed-product case can be located as follows. The total mass in suspension M_T must be the same in both cases 1 and 2 (without and with fines dissolving) if a Class II crystal system is assumed with recycling of dissolved fines. Thus, if both curves start out with the same density of nuclei $n_1^0 = n_2^0$, then curve 1 must have a slope intermediate between the slopes of the two sections of curve 2 in order for the integral of $L^3 n dL$ over the entire distribution to be equal in both cases. This locates curve 1 (qualitatively) in Fig. 8.3-1. As the drawdown time for case 1 is the same as τ_p in case 2, namely $\tau = V/Q_o$, it must be concluded that the growth rates are different, and in fact that $G_2 > G_1$. Thus, the net effect of fines removal is to force the growth rate to a higher level, producing the same production with crystals of larger average size having less total surface area. ♦

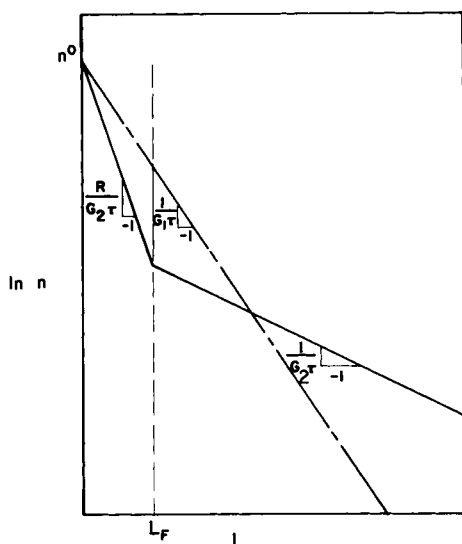


Fig. 8.3-1 Hypothetical population density plot (1) without (— — —) and (2) with (—) fines removal [after M. A. Larson, and A. D. Randolph, *Chem. Eng. Progr. Symp. Ser.* 95 65, 1 (1969)].

In practice, an unchanged density of nuclei after implementation of fines dissolution would only occur if the nucleation rate increased in the same proportion as growth rate, i.e., the nucleation sensitivity parameter i had the value of unity. If the higher supersaturation produced with fines removal results in a greater than proportionate increase in nucleation rate ($i > 1$), then additional nuclei will be formed, and size improvement will be somewhat less than expected based on the previous analysis. An estimate of size improvement could be made from Eq. (8.3-4) (point fines trap) where the fraction surviving the fines trap β is given as

$$\beta = \exp(-Q_F L_F / GV) \quad (8.3-7)$$

Actual CSD improvement with fines removal, including prediction of the bimodal weight distribution, could be obtained by solution of the equations of Section 8.1 with

$$C_w = R \quad \text{for } L < L_F$$

$$C_w = 1 \quad \text{for } L > L_F$$

$$C_p = 1 \quad \text{for all } L$$

together with actual physical parameters and kinetics of the particular system.

8.4 Classified Product Removal

Classified removal occurs when the mean retention probability of the particles varies over particle size ranges in which a significant fraction of the product mass is found. Removal of product-size crystals may be accelerated (decreased retention probability) or retarded (increased retention probability) relative to the mixed removal case, producing narrower or wider CSD's than the MSMPR distribution. Such product classification can occur inadvertently at the point of slurry removal in a mixed suspension, deliberately from a size-classified zone, or with ancillary process classification devices, e.g., wet screens, hydroclones, and eleutriators. An example of the first type is intermittent product removal from a vertical bootleg into which the larger crystals preferentially drift during the off portion of the cycle. Careful studies of solids removal from mixed slurries indicate that appreciable classification always occurs unless the slurry stream is removed isokinetically, i.e., at the same vector velocity as the circulating magma at the point of removal.

Deliberate product classification in the form of accelerated removal of product-size material is often used to narrow the CSD and, mistakenly, to increase particle size of the product by not removing so many fines. A mixed suspension crystallizer produces an inherently wide distribution of particle sizes, and it would seem that if all the crystals were left in the magma until they were of some large product size, say L_p , then a large and narrow CSD could indeed be produced. This case, representing ideal classification, has been thoroughly studied in comparison with the MSMPR mode of operation [1]. An interesting result of this comparison of mixed and perfectly classified modes of removal is that under comparable operating conditions when the MSMPR dominant size is equal to the classified particle size L_p , the MSMPR distribution contains approximately 11 times as many crystals per pound of product as the single-size classified crystals. Another way to express this comparison is that the classified case can tolerate only one-eleventh the nucleation rate as the mixed case and still produce the same dominant size. For this reason, product classification is almost always accompanied by size reduction unless nucleation is independently controlled; thus, classification to control the form of CSD and fines removal to influence particle size are often implemented together. In the mixed withdrawal case, many small crystals are withdrawn in the product before they are of appreciable size, which automatically serves as an effective means of population control at the price of producing a wider CSD.

Product classification can be rigorously simulated by the CSD algorithm of Section 8.1 utilizing the $C_p(L)$ function defined as the ratio of actual solids removal at size L to perfectly mixed removal. The $C_p(L)$ function can be obtained from analysis of experimental solids concentration data in both

suspension and withdrawal or as an idealized model of an external solids classifier. The latter is typically modeled simply as

$$\begin{aligned} C_w = C_p = 1 & \quad \text{for } L < L_p \\ C_w = C_p > 1 & \quad \text{for } L > L_p \end{aligned}$$

where L_p is the classification size at which significant deviation from mixed withdrawal begins. An idealized, yet realistic, model of a mixed-suspension, classified-product-removal crystallizer is given in the next example, in which product-size particles greater than size L_p are assumed to be removed at a rate z times those less than L_p in size. This model, representing a wet screen or hydroclone with a sharp cut point at size L_p and feed-to-undersize flow ratio of z , is idealized enough to permit analytic solution of the population balance, yet realistic enough to capture the quantitative effects of classification on CSD.

EXAMPLE 8.4-1 EFFECT OF CLASSIFICATION ON CSD

Construct a hypothetical semilog population density plot of CSD in a mixed-magma crystallizer before and after installation of a wet screen classifying device, classifying at particle size L_p . Refer to operation with and without the wet screen as cases 2 and 1, respectively. Assume density of nuclei remains constant. Physically, this would be true if the nucleation sensitivity parameter i is unity such that any changes in supersaturation brought about by classification result in proportionate changes in nucleation and growth rates and if nucleation is independent of the changes in solids concentration ($j=0$). A sharp classification at size L_p is assumed such that the idealized undersize and oversize particle drawdown times can be defined as

$$\begin{aligned} \tau_u = V/Q_o = \tau & \quad \text{for } L < L_p \\ \tau_p = V/zQ_o = \tau/z & \quad \text{for } L > L_p \end{aligned}$$

Solving for population density in the magma gives

$$\begin{aligned} (n_u)_2 &= k_1 \exp(-L/G_2 \tau_u) & \text{for } L < L_p \\ (n_p)_2 &= k_2 \exp(-L/G_2 \tau_p) & \text{for } L > L_p \end{aligned} \quad (8.4-1)$$

where k_1 and k_2 are constants. Continuity requires that $n_u(L_p) = n_p(L_p)$, giving the two straight-line segments shown in Fig. 8.4-1 having negative slopes $1/G_2 \tau$ and $z/G_2 \tau$ below and above the classification size L_p . Population

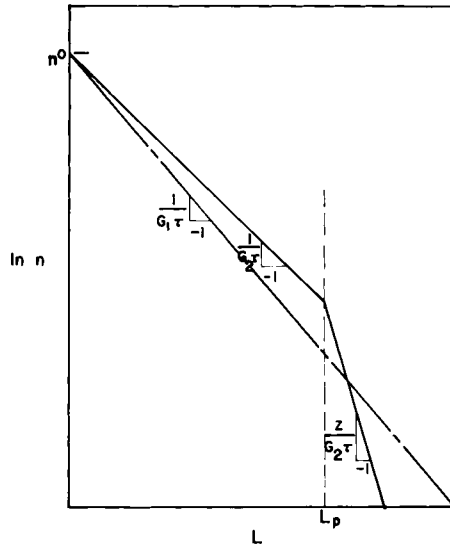


Fig. 8.4-1 Hypothetical population density plot (1) without (-----) and (2) with (——) classified product removal [after M. A. Larson, and A. D. Randolph, *Chem. Eng. Progr. Symp. Ser.* 95 65, 1 (1969)].

density for the MSMPR case is given by

$$n_1 = n^0 \exp(-L/G_1 \tau) \quad (8.4-2)$$

Location of the MSMPR line relative to the two segments of the classified-removal distribution depends on the classification size L_p . The integral of $L^3 n dL$ over the entire distribution is not the same for both cases, but is less for the case of classification, as the slurry density has been drawn down by the preferential removal of oversize crystals. However, a finer distribution has been produced having a greater specific surface area. Thus, total crystal area, the product of solids concentration times specific area, can either decrease or increase depending on the classification size. Typically, total crystal surface area will decrease. Thus, to produce the same production (Class II system), the growth rate is forced to a higher level and $G_2 > G_1$. This locates the curves as shown in Fig. 8.4-1. ♦

In the general case, nucleation will not increase in the same ratio as growth rate, as assumed in the above example, and the expected CSD with product classification can be calculated by the methods of Section 8.1 using empirical nucleation-growth rate kinetics. Analytic forms for CSD in suspension and

in product for the above classification model using power-law nucleation-growth rate kinetics are given in a subsequent example.

An ideal crystallizer would permit the separation, at will, of residence-time distributions of solids versus liquor and solids as a function of size. Thus, one could operate with arbitrary solids concentrations (by clear liquor overflow), produce a narrow CSD with classified removal, and keep nucleation in balance with a fines-destruction system. Low driving forces (supersaturation) would be maintained by the heavy retained seed bed intermediate in size between fines and product, L_F and L_P . Such a crystallizer could be realistically modeled using the idealizations in Examples 8.3-1 and 8.4-1.

EXAMPLE 8.4-2 CLASSIFIED REMOVAL WITH FINES DESTRUCTION

Construct a hypothetical semilog population density plot of CSD from a crystallizer with clear liquor removal, fines-destruction system, and classified product removal. Use the same idealizations as in the previous examples.

Fines destruction will give a large drawdown rate for crystals below size L_F . As a result, a plot of the fines size distribution will have a slope R times that of the crystal seed bed. This is shown by the first straight-line segment in Fig. 8.4-2. The second segment, representing the crystal seed bed, greater in size than fines but less than product crystals, decays with a negative slope

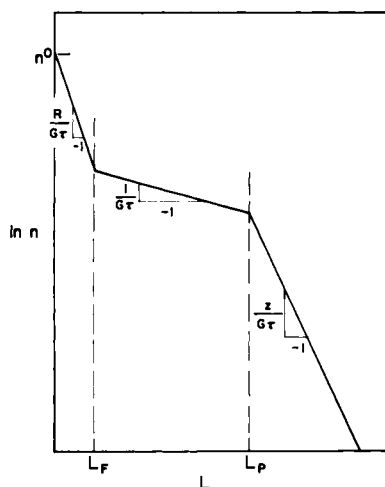


Fig. 8.4-2 Hypothetical population density plot with classified product removal and fines destruction [after M. A. Larson, and A. D. Randolph, *Chem. Eng. Progr. Symp. Ser.* 95 65, 1 (1969)].

of $1/G\tau$, where $\tau = V/Q_u$ and where Q_u , the underflow discharge rate, is determined by the amount of clear liquor overflow Q_o .

Accelerated product removal for sizes larger than L_p will give a drawdown in the third size range z times that of the seed-bed drawdown. This gives the final straight-line segment in Fig. 8.4-2, having a negative slope of $z/G\tau$.

Clear liquor overflow Q_o separates the residence time of solids relative to liquor, thus affecting the total solids concentration but not the form of CSD. Solids concentration is determined by the absolute slopes in Fig. 8.4-2, hence by the absolute value of Q_u . Clear liquor overflow must be taken into account in writing mass balances, but not population balances. Only slurry streams need be considered in the latter. ♦

As in previous examples, actual values of solids concentration M_T and crystal growth rate G can be found by simultaneous solution of population and mass balances together with nucleation-growth rate kinetics. A more realistic analysis of complex residence-time crystallizers can be made if actual drawdown rates as a function of size as well as accurate nucleation-growth rate kinetics in the resulting region of supersaturation are known for the system. It should be obvious from these examples that much remains to be learned about actual classification mechanics as well as nucleation-growth rate kinetics.

EXAMPLE 8.4-3 PREDICTION OF WEIGHT-SIZE DISTRIBUTION

Solve the associated population and mass balances of the idealized crystallizer of Fig. 8.4-2 together with power-law kinetics to predict CSD (weight basis) in the backmixed crystallizer and in the classified product. Assume an ideal fines trap removing particles at a rate $Q_F = (R-1)Q_u$ for $L < L_F$ and an ideal classifier removing product-size crystals at an accelerated rate zQ_u for $L > L_p$. The resultant population density plot was shown for this case in Fig. 8.4-2. Writing the distributions piecewise as shown in Fig. 8.4-2 yields

$$\begin{aligned} n_1 &= n^0 \exp(-RL/G\tau) & \text{for } L & \text{ in } (0, L_F) \\ n_2 &= C_1 \exp(-L/G\tau) & \text{for } L & \text{ in } (L_F, L_p) \\ n_3 &= C_2 \exp(-zL/G\tau) & \text{for } L & \text{ in } (L_p, \infty) \end{aligned} \quad (8.4-3)$$

where $\tau = V/Q_u$. Continuity of the magma distribution requires that $n_1(L_F) = n_2(L_F)$ and $n_2(L_p) = n_3(L_p)$. (Note: Continuity of the product distribution is not required and does not hold with the discontinuous changes in withdrawal rate of this example.) Making the dimensionless substitutions $x = L/G\tau$ and $y = n/n_0^0$ and evaluating the constants gives the dimensionless population

distributions

$$\begin{aligned} y_1 &= \exp(-Rx) \\ y_2 &= \exp[-(R-1)x_1] \exp(-x) \\ y_3 &= \exp[-(R-1)x_1] \exp[(z-1)x_2] \exp(-zx) \end{aligned} \quad (8.4-4)$$

where $x_1 = L_F/G\tau$ and $x_2 = L_p/G\tau$.

From the definition of product weight distribution in suspension and product,

$$W(x) = \int_0^x x^3 y \, dx / \int_0^\infty x^3 y \, dx \quad (8.4-5)$$

$$W_P(x) = \int_0^x Q^P(x) x^3 y \, dx / \int_0^\infty Q^P(x) x^3 y \, dx \quad (8.4-6)$$

These integrals must be broken up into three parts for integration along the three segments of the distribution curve. Define the dimensionless arguments

$$\begin{aligned} p &= RL/G\tau, & x &= L/G\tau, & q &= zL/G\tau \\ p_1 &= RL_F/G\tau, & x_1 &= L_F/G\tau, & x_2 &= L_p/G\tau, & q_2 &= zL_p/G\tau \end{aligned}$$

Then, in terms of the dimensionless weight distribution function $w(x) = \frac{1}{6} \int_0^x p^3 e^{-p} dp$ (as tabulated in Appendix A), the cumulative weight distributions in suspension and product are given as

$$\begin{aligned} W(L) &= w(p)/R^4 D \\ W_P(L) &= w(p)/R^4 D_P \end{aligned} \quad \text{for } L < L_F \quad (8.4-7)$$

$$\begin{aligned} W(L) &= W(L_F) + \frac{\{\exp[-(R-1)x_1]\} [w(x) - w(x_1)]}{D} \\ W_P(L) &= W_P(L_F) + \frac{\{\exp[-(R-1)x_1]\} [w(x) + w(x_1)]}{D_P} \end{aligned} \quad \begin{array}{l} \text{for } L \\ \text{in } (L_F, L_p) \end{array} \quad (8.4-8)$$

$$\begin{aligned} W(L) &= W(L_p) + \frac{\{\exp[(z-1)x_2 - (R-1)x_1]\} [w(q) - w(q_2)]}{z^4 D} \\ W_P(L) &= W_P(L_p) + \frac{\{\exp[(z-1)x_2 - (R-1)x_1]\} [w(q) - w(q_2)]}{z^3 D_P} \end{aligned} \quad \begin{array}{l} \text{for } L \\ \text{in } (L_p, \infty) \end{array} \quad (8.4-9)$$

The dimensionless denominators D and D_p are given as

$$D = \frac{w(p_1)}{R^4} + \{\exp[-(R-1)x_1]\} [w(x_2) - w(x_1)] \\ + \frac{\{\exp[(z-1)x_2 - (R-1)x_1]\} [1 - w(q_2)]}{z^4} \quad (8.4-10)$$

$$D_p = \frac{w(p_1)}{R^4} + \{\exp[-(R-1)x_1]\} [w(x_2) - w(x_1)] \\ + \frac{\{\exp[(z-1)x_2 - (R-1)x_1]\} [1 - w(q_2)]}{z^3} \quad (8.4-11)$$

Equations (8.4-7)–(8.4-9) give the form of CSD for this complex process configuration; actual sizes must be determined by solving for the growth rate G which satisfies a mass balance for the process. Production rate is given in terms of the population distribution as

$$P = \rho k_v \int_0^\infty Q^p(L) n L^3 dL \quad (8.4-12)$$

Only one value of G will give an $n(L)$ that satisfies the above constraint. Writing out the above constraint in terms of the parameters of the system gives

$$P/\rho k_v = 6n_0^0 Q_u (G\tau)^4 \{ [w(p_1)/R^4] + \{\exp[-(R-1)x_1]\} [w(x_2) - w(x_1)] \\ + (1/z^3) \{\exp[-(R-1)x_1 + (z-1)x_2]\} [1 - w(q_2)] \} \quad (8.4-13)$$

Inserting the power-law form of the density of nuclei $n^0 = k_N G^{i-1}$ gives

$$G^{i+3} = P/6\rho k_v k_N \tau^4 D(G) Q_u \quad (8.4-14)$$

where $D(G)$ is a growth-rate-dependent term given by Eq. (8.4-10). Rearranging gives

$$G = [P/6\rho k_v k_N \tau^4 D(G) Q_u]^{1/(i+3)} = F(G) \quad (8.4-15)$$

The above equation can be solved by standard trial-and-error methods for the correct value of G which satisfies this mass balance. The weight distribution equation can then be solved with this value of G to observe the effects

of changes in dissolving and product classification on product weight-size distribution. Note that the retention time τ in Eq. (8.4-15) was based on underflow Q_u . Changes in clear liquor removal affect Q_u , hence G . Thus, the particle size, but not the basic form of CSD, is altered by clear liquor removal. ♦

The CSD equations of Example 8.4-3 can be used to predict actual weight distributions for the idealized fines-dissolving and product classification examples 8.3-1, 8.4-1, and 8.4-2. These models are idealized, yet realistic enough to be useful in assessing the probable interaction of process configuration with given system kinetics to alter CSD. The five parameters defining possible process configurations are the fines-removal ratio R , product-removal ratio z , maximum fines-removal size L_F , product classification size L_p , and the ratio of clear liquor overflow to mixed underflow Q_o/Q_u . Fines-removal and/or product classification is simulated when R and/or z are greater than unity for reasonable values of the parameters L_F and L_p . When $R = z = 1$, the equations coalesce to the growth-type MSMR case.

8.5 Crystallizer Cascades

Crystal-size distribution can be markedly altered by crystallizing in a series of crystallizer bodies such that the entire magma flows from one stage to another. Various strategies can be employed to alter the CSD. Among these are conditions which permit nucleation in the first stage but only growth in the second, and the use of classified product removal from each stage. It is more realistic, however, to recognize that both nucleation and growth will take place in each stage and that classified product removal increases the tendency toward instability.

Relatively simple design measures can be taken to alter CSD, however, by arbitrarily fixing different retention times in each stage and fixing different production rates in each stage. For cooling systems, the former is accomplished by using different body sizes in the cascade and the latter is accomplished by imposing different rates of energy removal on each stage.

Our objectives in this section are to show what CSD could result from various operating conditions. We will first give the applicable material and population balance equations for a cascade, then cast these equations in dimensionless form for ease in manipulation. As discussed in Section 8.1, cascaded crystallizers can be described by the general CSD algorithm. Here, however, we examine the special case of equal flows, no fines destruction, and unclassified product removal to illustrate the fundamental behavior of cascaded systems. Two- and three-stage cascade systems will then be used to illustrate the effects of these constraints on CSD.

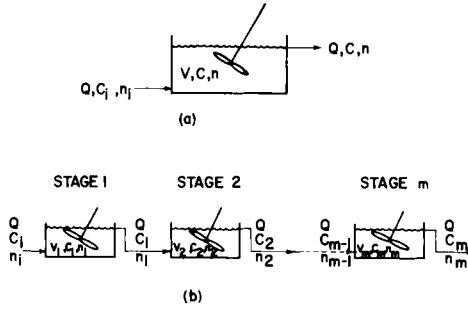


Fig. 8.5-1 (a) Single stage. (b) Cascade system.

Consider a cascade of m well-stirred stages operated so that no seeding is required in stage 1 and the entire slurry is carried forward to each subsequent stage as shown in Fig. 8.5-1. A steady-state number balance around each stage results in

$$\begin{aligned} V_1 [d(G_1 n_1)/dL] &= -Q_1 n_1 \\ V_2 [d(G_2 n_2)/dL] &= Q_1 n_1 - Q_2 n_2 \\ V_m [d(G_m n_m)/dL] &= Q_{m-1} n_{m-1} - Q_m n_m \end{aligned} \quad (8.5-1)$$

A mass balance on the solute crystallized in each stage gives

$$\begin{aligned} Q_1 C_1 &= Q_1 C_1 + \rho k_v Q_1 \int_0^\infty n_1 L^3 dL \\ Q_{m-1} C_{m-1} &= Q_m C_m + \rho k_v Q_m \int_0^\infty n_m L^3 dL \end{aligned} \quad (8.5-2)$$

From the previous development in Section 4.5 for a single stage, Eq. (8.5-2) can be rearranged to give the following constraint on growth rate:

$$G_j = [(C_{j-1} Q_{j-1} / Q_j) - C_j] / \left[3k_v \rho (V_j / Q_j) \int_0^\infty n_j L^2 dL \right], \quad j = 1, \dots, m \quad (8.5-3)$$

The nucleation and growth kinetics expressed as before are

$$(n^0)_j = k_N G_j^{i-1} \quad (8.5-4)$$

When Q_j is the same for all j , the set to be solved is

$$V_j[d(G_j n_j)/dL] = Q(n_{j-1} - n_j)$$

[from Eq. (8.5-2)];

$$G_j = \delta C_j / \left(3k_v \rho \tau_j \int_0^\infty n_j L^2 dL \right) \quad (8.5-5)$$

and Eq. (8.5-4),

$$(n^0)_j = k_N G_j^{i-1}$$

where $j = 1, 2, \dots, m$.

The effects of staging on CSD can best be illustrated by comparing the CSD with that expected from a single-stage system for the same system retention time and production. To do this, it is necessary to define a set of dimensionless variables and cast Eqs. (8.5-2), (8.5-4), and (8.5-5) in dimensionless form. These variables will be slightly different from those previously used. They are defined in Table 8.5-1.

Table 8.5-1
Dimensionless Variables

Variable	Dimensionless symbol	Single-stage symbol	j th stage symbol	Dimensionless definition
Size	x	L	L	LQ/GV
Number density	y_j	n	n_j	n_j/n^0
Density of nuclei	y_j^0	n^0	n_j^0	n_j^0/n^0
Crystal surface area	α_j	A	A_j	A_j/A
Growth rate	ρ_j	G	G_j	G_j/G
Production	σ_j	δC	δC_j	$\delta C_j/\delta C$
Body volume	γ_j	V	V_j	V_j/V
Flow	q_j	Q	Q_j	Q_j/Q

For the purpose of the subsequent development, it will be assumed that the kinetic parameters for each of the j stages are identical to those in the single-stage reference case. That is, they are independent of temperature. For cooling systems, we assume Q_j is a constant, and therefore q_j is 1 and the parameter characterizing retention time in each stage is γ_j . The definitions of γ_j and σ_j require that

$$\sum_{j=1}^m \gamma_j = 1, \quad 0 < \gamma_j < 1 \quad (8.5-6)$$

$$\sum_{j=1}^m \sigma_j = 1, \quad 0 < \sigma_j < 1$$

Using the substitutions given in Table 8.5-1, Eqs. (8.5-2), (8.5-4), and (8.5-5) become

$$\rho_j \gamma_j (dy_j/dx) = y_{j-1} - y_j, \quad \rho_j = \sigma_j / \gamma_j \alpha_j, \quad y_j^0 = \rho_j^{i-1} \quad (8.5-7)$$

In addition, dimensionless area α_j is defined by

$$\alpha_j = \int_0^\infty y_j x^2 dx / \int_0^\infty y x^2 dy = \frac{1}{2} \int_0^\infty y_j x^2 dx \quad (8.5-8)$$

Equations (8.5-7) and (8.5-8) along with constraint (8.5-6) define the problem. The choice parameters are γ_j and σ_j , representing the stage retention time and the stage production rate, respectively.

Before considering the CSD obtained from staged systems, we now repeat the solution of the single-stage equation for the size distribution. For $m = 1$, the solutions are

$$y = \exp(-x), \quad \alpha = 1, \quad \rho = 1 \quad (8.5-9)$$

the cumulative mass distribution is [Eq. (4.4-9)]

$$W = 1 - \exp(-x) (1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3)$$

and the differential mass distribution function is Eq. (4.4-13)]

$$w = x^3 \exp(-x)/6$$

Equation (4.4-13), previously plotted in Fig. 4.4-1, is plotted in subsequent sections for comparison purposes with distributions obtained from staged systems.

With no attempt to be exhaustive, we now give several examples of the size distribution expected from two- and three-stage systems.

EXAMPLE 8.5-1

Consider a two-stage cascade with nucleation in the first stage only. Assume equal-size bodies and equal production rates. Therefore, $\sigma_1 = \sigma_2 = \frac{1}{2}$, $\gamma_1 = \gamma_2 = \frac{1}{2}$.

Stage 1:

$$y_1 = y_1^0 \exp(-2x/\rho_1), \quad y_1^0 = \rho_1^{i-1}, \quad \rho_1 = 1/\alpha_1, \quad \alpha_1 = y_1^0 (\rho_1/2)^3 \quad (8.5-10)$$

Stage 2:

$$\begin{aligned}
 y_2 &= y_1^0 [\rho_1 / (\rho_1 - \rho_2)] [\exp(-2x/\rho_1) - \exp(-2x/\rho_2)], & y_2^0 &= 0 \\
 \alpha_1 &= y_1^0 [\rho_1 / (\rho_1 - \rho_2)] \{[\rho_1/2]^3 - [\rho_2/2]^3\} \\
 W_2 &= y_1^0 [\rho_1 / (\rho_1 - \rho_2)] \{[(\rho_1^4 - \rho_2^4)/2^4] + \exp(-2x/\rho_2) \\
 &\quad \times [(\rho_2/2)^4 + (\rho_2/2)^3 x + \frac{1}{2}(\rho_2/2)^2 x^2 + \frac{1}{6}(\rho_2/2) x^3] \\
 &\quad - \exp(-2x/\rho_1) [(\rho_1/2)^4 + (\rho_1/2)^3 x + \frac{1}{2}(\rho_1/2)^2 x^2 + \frac{1}{6}(\rho_1/2) x^3]\} \\
 w_2(x) &= y_1^0 [\rho_1 / (\rho_1 - \rho_2)] (x^3/6) [\exp(-2x/\rho_1) - \exp(-2x/\rho_2)]
 \end{aligned} \tag{8.5-11}$$

The distribution $w_2(x)$ for stage 2 is plotted in Fig. 8.5-2 along with the distribution for a single stage.

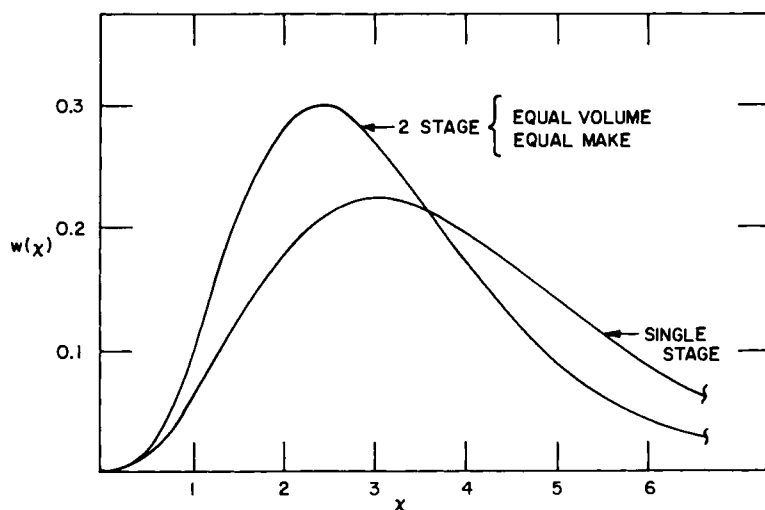


Fig. 8.5-2 Mass distribution for a two-stage system with equal volumes and equal make (no nucleation in Stage 2).

The normalized growth rate for a single stage is unity, by Eq. (8.5-9). From Eqs. (8.5-10), we get for stage 1 of this two-stage system the dimensionless growth rate

$$\rho_1 = (8)^{1/(3+i)} \tag{8.5-12}$$

Under the assumed conditions, the growth rate must always be greater in stage 1 than in a single-stage system. ♦

EXAMPLE 8.5-2

Consider two stages with conditions such that the growth rates are equal and the retention times are equal.

This necessarily means that the production rate in stage 2 would be greater than in stage 1 because of the greater surface area available for deposition of solute.

The solution for the first stage is identical to that in Example 8.5-1 except for the mass balance relationship. Here,

$$\rho_1 = 2\sigma_1/\alpha_1 \quad (8.5-13)$$

and

$$\rho_1 = \rho_2, \quad \sigma_1 < \sigma_2 \quad (8.5-14)$$

For stage 2:

$$\begin{aligned} y_2 &= y_1^0 (2x/\rho) \exp(-2x/\rho) + y_2^0 \exp(-2x/\rho) \\ \rho_2 &= 2\sigma_2/\alpha_2, \quad \alpha_2 = (3y_1^0 + y_2^0) (\rho/2)^3 \end{aligned} \quad (8.5-15)$$

$$\begin{aligned} W_2 &= y_2^0 \{(\rho/2)^4 - \exp(-2x/\rho) [(\rho/2)^4 + (\rho/2)^3 x \\ &\quad + \frac{1}{2}(\rho/2)^2 x^2 + \frac{1}{6}(\rho/2) x^3]\} \\ &\quad + 4y_1^0 (2/\rho) \{(\rho/2)^5 - \exp(-2x/\rho) [(\rho/2)^5 + (\rho/2)^4 x \\ &\quad + \frac{1}{2}(\rho/2)^3 x^2 + \frac{1}{6}(\rho/2)^2 x^3 + \frac{1}{24}(\rho/2) x^4]\} \\ w_2 &= (x^3/6) [y_1^0 (2x/\rho) \exp(-2x/\rho) + y_2^0 \exp(-2x/\rho)] \end{aligned}$$

Figure 8.5-3 compares the mass distribution obtained from a single stage with that for a two-stage system with equal growth rates for a system with nucleation order 2 and with nucleation in both vessels. These plots again show a smaller mean crystal size in a two-stage system but little change in the coefficient of variation.

Note that the fraction of production required in stage 2 to achieve this result is

$$\sigma_2 = \sigma_1(\alpha_2/\alpha_1) \quad \blacklozenge \quad (8.5-16)$$

EXAMPLE 8.5-3

The following solution is for an arbitrary allocation of production and retention time in a two-stage crystallizer for a Class II system. Solutions are given for the number distribution, the area, and the growth rate. The assumed

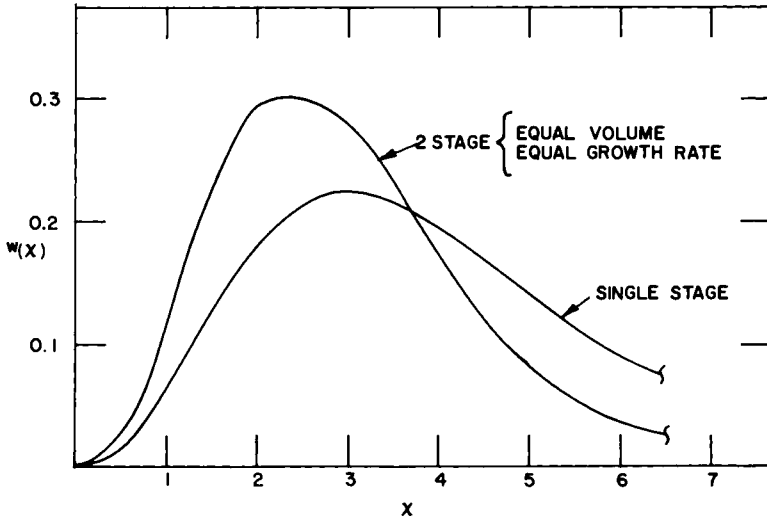


Fig. 8.5-3 Mass distribution for a two-stage system with equal volumes and equal growth rates (nucleation in both stages).

kinetics are continuous over the range of supersaturation and the nucleation kinetics are assumed independent of solids in suspension. The mass distribution is not given because of its complexity.

For stage 1:

$$\begin{aligned} y_1 &= y_1^0 \exp(-x/\rho_1 \gamma_1), & \alpha_1 &= y_1^0 (\sigma_1/\alpha_1)^3 \\ \rho_1 &= \sigma_1/\alpha_1 \gamma_1, & y_1^0 &= \rho_1^{i-1} \end{aligned} \quad (8.5-17)$$

For stage 2:

$$\begin{aligned} y_2 &= y_2^0 \exp(-x/\rho_2 \gamma_2) + y_1^0 [\rho_1 \gamma_1 / (\rho_1 \gamma_1 - \rho_2 \gamma_2)] \\ &\quad \times [\exp(-x/\rho_1 \gamma_1) - \exp(-x/\rho_2 \gamma_2)] \\ \alpha_2 &= y_2^0 (\sigma_2/\alpha_2)^3 + (y_1^0 \sigma_1/\alpha_1) \\ &\quad \times [(\sigma_2^2/\alpha_2^2) + (\sigma_1 \sigma_2/\alpha_1 \alpha_2) + (\sigma_1^2/\alpha_1^2)] \\ \rho_2 &= \sigma_2/\alpha_2 \gamma_2, & y_2^0 &= \rho_2^{i-1} \end{aligned} \quad (8.5-18)$$

We give here, for completeness, the solution for the third stage of a three-stage cascade with arbitrary allocation of total crystal volume and production

in each stage:

$$\begin{aligned}
 y_3 &= y_3^0 \exp\left(-\frac{x}{\rho_3 \gamma_3}\right) + y_2^0 \left(\frac{\rho_2 \gamma_2}{\rho_2 \gamma_2 - \rho_3 \gamma_3}\right) \\
 &\quad \times \left[\exp\left(-\frac{x}{\rho_2 \gamma_2}\right) - \exp\left(-\frac{x}{\rho_3 \gamma_3}\right) \right] \\
 &\quad + y_1^0 \left\{ \frac{\rho_1^2 \gamma_1^2}{(\rho_1 \gamma_1 - \rho_2 \gamma_2)(\rho_2 \gamma_2 - \rho_3 \gamma_3)} \right. \\
 &\quad \times \left[\exp\left(-\frac{x}{\rho_1 \gamma_1}\right) - \exp\left(-\frac{x}{\rho_3 \gamma_3}\right) \right] \\
 &\quad - \frac{\rho_1 \rho_2 \gamma_1 \gamma_2}{(\rho_1 \gamma_1 - \rho_2 \gamma_2)(\rho_2 \gamma_2 - \rho_3 \gamma_3)} \\
 &\quad \times \left. \left[\exp\left(-\frac{x}{\rho_2 \gamma_2}\right) - \exp\left(-\frac{x}{\rho_3 \gamma_3}\right) \right] \right\} \\
 \alpha_3 &= y_1^0 \left(\frac{\rho_1^2 \gamma_1^2}{\rho_1 \gamma_1 - \rho_2 \gamma_2} \right) \left(\frac{\sigma_1^2}{\alpha_1^2} + \frac{\sigma_1 \sigma_3}{\alpha_1 \alpha_3} + \frac{\sigma_3^2}{\alpha_3^2} \right) \\
 &\quad - \left[y_1^0 \frac{\rho_1 \rho_2 \gamma_1 \gamma_2}{(\rho_1 \gamma_1 - \rho_2 \gamma_2)} - y_2^0 \rho_2 \gamma_2 \right] \left(\frac{\sigma_2^2}{\alpha_2^2} + \frac{\sigma_2 \sigma_3}{\alpha_2 \alpha_3} + \frac{\sigma_3^2}{\alpha_3^2} \right) \\
 &\quad + y_3^0 \frac{\sigma_3^3}{\alpha_3^3} \\
 \rho_3 &= \frac{\sigma_3}{\alpha_3 \gamma_3}
 \end{aligned} \tag{8.5-19}$$

The implicit nature of these quantities makes them difficult to evaluate. However, the above equations define the system. The nomenclature listed in Table 8.5-1 applies to all previous examples and the system described by Eqs. (8.5-7) and (8.5-8).

In many instances, secondary nucleation effects must be considered. These may be handled by using the power-law model (8.2-7),

$$n^0 = k_N G^{i-1} M_T^j$$

Here, we assume the phenomenon of secondary nucleation is related to the solids density. In dimensionless form, this becomes, for the k th stage,

$$(y^0)_k = (\rho)_k^{i-1} (\sigma)_k^j \tag{8.5-20}$$

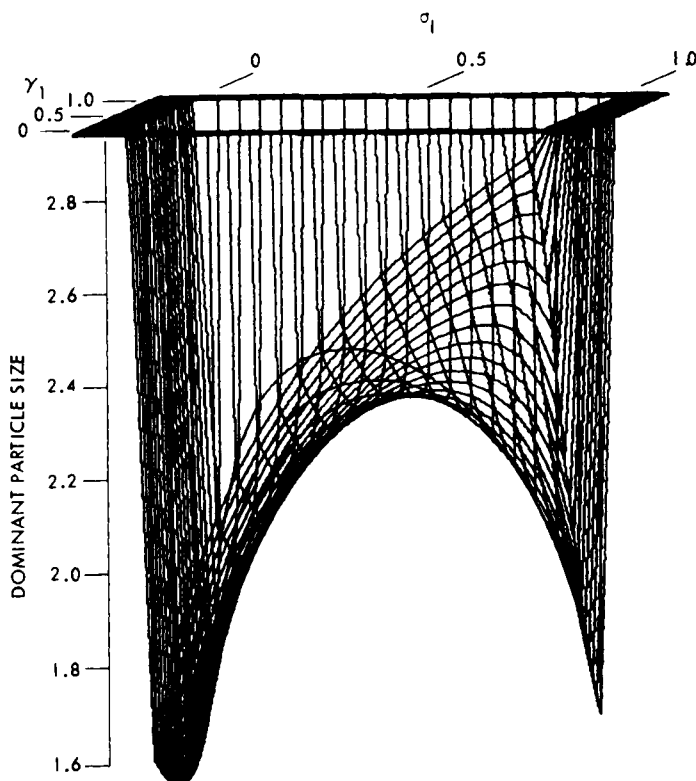


Fig. 8.5-4 Dominant particle size for a two-stage crystallizer of arbitrary makes σ_1 and σ_2 ($\sigma_1 + \sigma_2 = 1$) and arbitrary volumes γ_1 and γ_2 ($\gamma_1 + \gamma_2 = 1$) [after P. R. Wolff, and M. A. Larson, *Chem. Eng. Progr. Symp. Ser. 110* 67, (1971)].

All previous solutions still apply except that nuclei population densities are replaced by $\rho^{i-1} \sigma^j$ instead of ρ^{i-1} when calculations are made.

Figure 8.5-4 is a plot of dimensionless dominant particle size for a two-stage Class II cascaded system. In this example a secondary nucleation model was used. The independent variables γ_1 and σ_1 are respectively the fraction of the total residence time and the production allocated to the first stage. Note that the dimensionless dominant particle size x_d has the value of three for a one-stage system and that the dominant size produced in this two-stage system is less than in the single-stage case. ♦

8.6 Batch Crystallizers

The emphasis throughout this volume has been on continuous systems although many crystallization processes are operated as batch processes. Here, we briefly consider the modeling of the CSD from batch processes operating under certain constraints. The models developed suggest various modes of operation which will produce various CSD.

The solution of these equations is somewhat more involved and the limitations on the use of the resulting models are greater because the CSD is now time-dependent as well as size-dependent. As a consequence, in the development of the model, we must solve partial differential equations. Further, the initial conditions applicable for a batch operation are not well understood even for seeded batch operations. The CSD obtained from these models are highly dependent on initial conditions; therefore, the results given here must be regarded only as illustrations of the analysis and not as expected CSD from operating crystallizers.

A batch system or unseeded semibatch system has no net inflow or outflow of crystals; therefore, the population balance, Eq. (3.5-10), reduces to

$$\partial(nV)/\partial t + \partial(nGV)/\partial L = 0 \quad (8.6-1)$$

Because the working volume of a batch or semibatch system may be time-varying, it is convenient to redefine the number density on the basis of the total operating volume of the system such that

$$\bar{n} = nV \quad (8.6-2)$$

With this substitution, Eq. (8.6-1) reduces to

$$\partial\bar{n}/\partial t + \partial(G\bar{n})/\partial L = 0 \quad (8.6-3)$$

Assuming a power-law nucleation model of order i , the population density of nuclei becomes

$$\bar{n}^0(t) = k_N G^{i-1} V \quad (8.6-4)$$

The mass balance for a batch system is

$$C(dV/dt) + (dW/dt) = 0 \quad (8.6-5)$$

where W is the mass of solids in suspension and C is the concentration of solute in solution. The mass balance for a semibatch system (i.e., a system having a continuous feed) would contain an additional term for solute input.

The moment equations applicable are

$$\begin{aligned} d\bar{N}/dt &= k_N G^i V, & d\bar{\mathcal{Z}}/dt &= \bar{N}G \\ d\bar{A}/dt &= 2k_a \bar{\mathcal{Z}}G, & d\bar{W}/dt &= (3k_v/k_a) \bar{A}G \end{aligned} \quad (8.6-6)$$

If an initial condition for the size distribution $[\bar{n} = \bar{n}(0, L)]$ is known or can be assumed, Eqs. (8.6-3)–(8.6-6) can be solved to give the CSD from a batch or semibatch system as a function of batch time.

EXAMPLE 8.6-1 CONSTANT-GROWTH-RATE, EVAPORATIVE SYSTEM

For a variable-volume, completely mixed, batch evaporative crystallizer, subject to the condition of constant growth rate, Eq. (8.6-3) becomes

$$\frac{\partial \bar{n}}{\partial t} + G \frac{\partial \bar{n}}{\partial L} = 0 \quad (8.6-7)$$

Using Eq. (8.6-7) in the moment equations (8.6-6) and combining the moment equations with the mass balance equation (8.6-5) gives

$$d^4 V/dt^4 + 4a^2 V = 0 \quad (8.6-8)$$

where the constant $4a^2 = 6k_v k_N G^{i+3}/C$.

Arbitrarily assuming the initial conditions on the moments to be zero and $V = V_0$ results in the following initial conditions for Eq. (8.6-8):

$$V(0) = V_0, \quad \dot{V}(0) = \ddot{V}(0) = \ddot{V}(0) = 0$$

The solution to Eq. (8.6-8) is then

$$V(t) = V_0 (\cos at) (\cosh at) \quad (8.6-9)$$

Equation (8.6-9) represents the time variance of the volume needed to produce a constant growth rate over the duration of the batch operation. If the rate of volume change is related to the energy input rate Q by

$$dV/dt = -Q/\rho\lambda \quad (8.6-10)$$

then the rate of energy input necessary to maintain a constant growth rate is

$$Q = V_0 \rho\lambda [(\sin at) (\cosh at) - (\cos at) (\sinh at)] \quad (8.6-11)$$

The solution of the set of equations for the size distribution is

$$\bar{n} = \bar{n}^0 \{ [\cos(a/G)] (Gt - L) \} \{ [\cosh(a/G)] (Gt - L) \} [1 - U(L - Gt)] \quad (8.6-12)$$

The quantity $1 - U(L - Gt)$ is equal to one for $L < Gt$ and equal to zero for $Gt > L$. Plots of $\bar{n}/\bar{n}^0$ versus $L/G\tau_f$ are given in Fig. 8.6-1 for various values of $\theta = t/\tau_f$, where τ_f is the total length of time for the batch operation. The population density of nuclei decreases with time because the volume of the mother liquor decreases. ♦

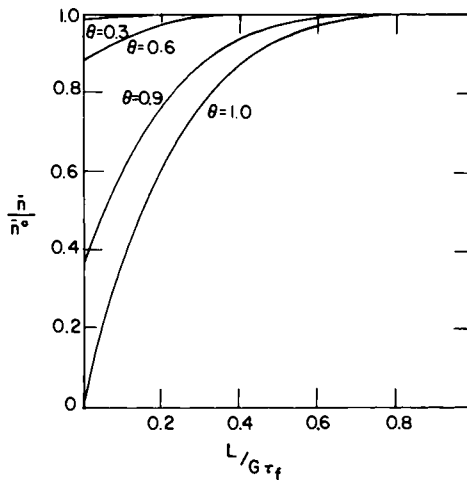


Fig. 8.6-1 Predicted CSD from a batch system operated under the constraint of Example 8.6-1 [after J. B. Baliga, Crystal nucleation and growth kinetics in batch evaporative crystallization, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1970, unpublished].

The distributions shown in Fig. 8.6-1 are seldom if ever observed in real crystallizers because the initial condition used for the CSD, namely zero, is seldom applicable. Further, it is difficult to maintain a constant growth rate in practice.

In any real crystallizer, initial nucleation can occur by several mechanisms and usually occurs as an initial shower. This being the case, one cannot realistically use the zero initial condition on the size distribution. In reality, an initial distribution exists and subsequent nucleation is normally of the secondary type.

In experiments using a small evaporative crystallizer to crystallize potassium sulfate, Baliga [2] used the size distribution of crystals in suspension at the

time of first appearance of crystals as an initial CSD. This distribution is shown in Fig. 8.6-2. The system was operated at constant heat load and consequently at a constant evaporation rate. The plots in Fig. 8.6-3 show how the size distribution changed as time progressed.

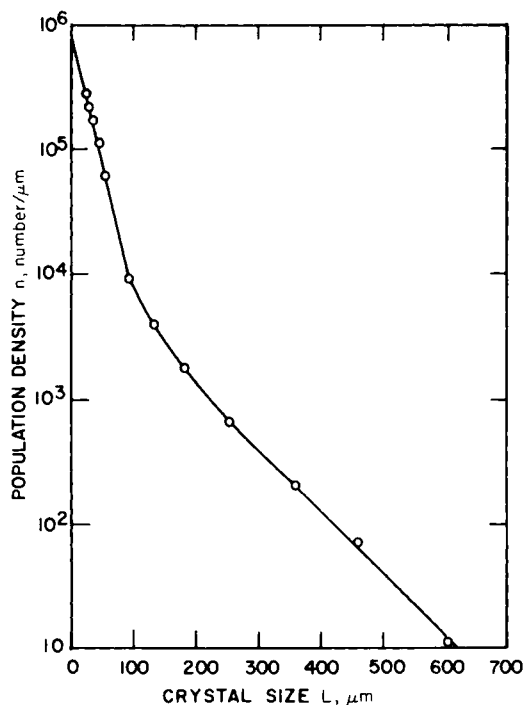


Fig. 8.6-2 Initial CSD for batch crystallization of K_2SO_4 [after J. B. Baliga, Crystal nucleation and growth kinetics in batch evaporative crystallization, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1970, unpublished].

The set of equations (8.6-3)–(8.6-6) were solved numerically using the distribution of Fig. 8.6-2 to provide the initial conditions. Here, the growth rate was allowed to vary in time as required by the mass balance. The results are shown in Fig. 8.6-4. In order to fit the shape of the experimental curve, it was necessary to recognize that the growth rate of potassium sulfate varies with size. The growth function then took on the form

$$G = G^0(t)g(L) \quad (8.6-13)$$

where $G^0(t)$ represents the growth-rate dependence on the time variance of

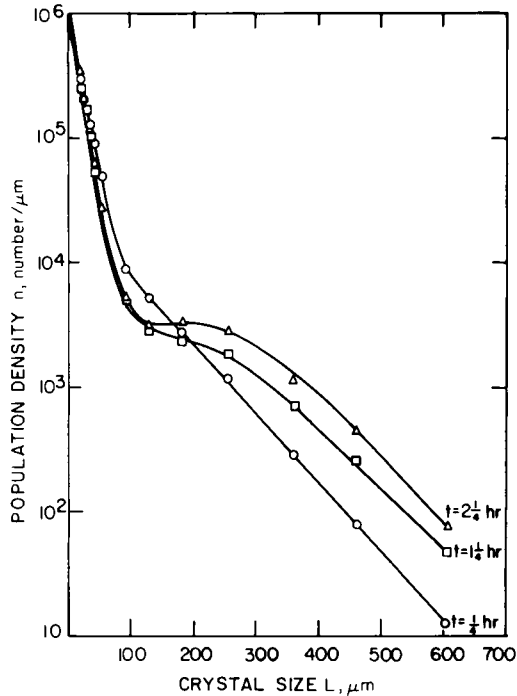


Fig. 8.6-3 CSD at various times for batch crystallization [after J. D. Baliga, Crystal nucleation and growth kinetics in batch evaporative crystallization, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1970, unpublished].

supersaturation and $g(L)$ represents the time variance of growth due to crystal size. The results agreed qualitatively with experiment.

8.7. Summary

The CSD obtained from a crystallization system is determined not only by the relative kinetics of nucleation and growth, but also by the relative residence times of the various sizes of crystals. Various operation strategies have been shown to affect the size distribution. The effects of preferential removal of fines and their subsequent destruction as well as the effects of classified product removal were demonstrated. In addition, it was shown that cascades without classification can also markedly affect size distribution. Finally, the batch crystallizer was briefly discussed to show how the variation of residence times of the crystals affects the CSD from these systems.

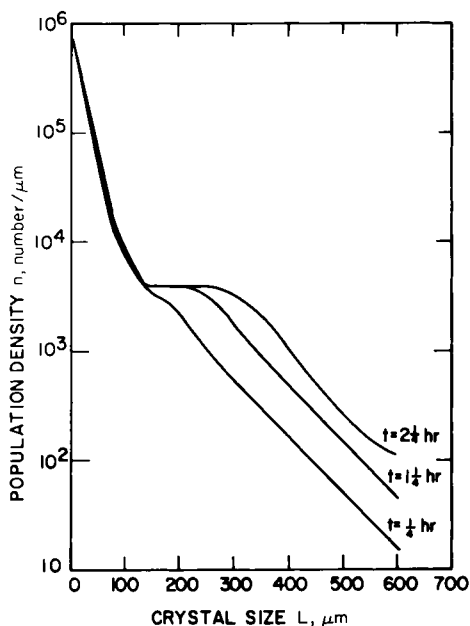


Fig. 8.6-4 Computed CSD using initial condition from Fig. 8.6-2 [after J. D. Baliga, Crystal nucleation and growth kinetics in batch evaporative crystallization, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1970, unpublished].

In the design of crystallization systems, the requirements on the product CSD coupled with the fundamental kinetics of the system will determine the residence-time allocations which must be used.

All of the examples chosen in this chapter have been taken from the area of crystallization; similar effects of residence-time distribution are observed in other particulate processes. The techniques of this chapter are still valid and the effects of residence-time distribution alter the form of a one-dimensional distribution in the same qualitative way when the internal coordinate is linearly related to age in the environment as in the case of particle size in crystallization. However, there is a large interaction between residence-time distribution and system kinetics; thus, specific results must be obtained through solution of the appropriate population and mass balance equations.

References

1. W. C. Saeman, *AIChE J.* **2**, 107 (1956).
2. J. B. Baliga, Crystal nucleation and growth kinetics in batch evaporative crystallization, Ph.D. Thesis, Iowa State Univ., Ames, Iowa, 1970, unpublished.

KINETIC DATA FROM MSMPR CRYSTALLIZERS

Published kinetic data for use in the CSD design of industrial crystallization systems are rare and generally of questionable applicability. Such data are for the most part taken at process conditions greatly different from conditions existing in industrial crystallizers. The greatest difficulty with most published data is that the rates of nucleation and growth were measured separately under different conditions. Theoretical relationships based on homogeneous mechanisms are of limited value as well, because these mechanisms seldom obtain in industrial systems.

Until more is known about nucleation and growth rate phenomena, it will be necessary to generate experimentally the necessary data for specific applications. In this chapter, we demonstrate how the analysis presented in the previous chapters can be used with the appropriate experimental procedure to develop kinetic expressions and to measure the effects of process conditions on the kinetics of crystallization in realistic crystallization environments approximating those in industrial practice. We will discuss here how the continuous mixed-suspension, mixed-product-removal (MSMPR) crystallizer can be used to generate growth and nucleation data. Such systems have the advantage that conditions similar to those in industrial-size units can be attained. The most important advantage is that the technique permits the measurement of both nucleation and growth rates simultaneously at the same level of supersaturation, level of agitation, temperature, and suspension density.

In the final paragraphs of the chapter, we present experimental data for various systems obtained by the technique. The conditions under which the data were taken are carefully defined. It should be emphasized that the use of these data and these kinetic expressions should be made with caution if the application conditions are greatly different from the experimental conditions.

9.1 Features of the Apparatus

In order to meet the requirements made by the assumptions inherent in the derivation of the size distribution equation, the experimental apparatus must exhibit at least the following features:

- a. The crystallizer must be designed so that both the suspension and the mother liquor are well-mixed, i.e., the liquor composition and the crystal-size distribution must be uniform throughout the volume of the vessel. This should be accomplished with a minimum power input by the agitator.
- b. Slurry discharge must be accomplished so that the discharge suspension density, size distribution, and liquor composition are the same as they are in the crystallizer. There should be no size classification at the discharge.
- c. The vessel must be small enough so that minimum feed material is required but large enough so that sampling does not result in appreciable disturbance to the system. Sieving is the most typical method for the determination of the size distribution; therefore, the sample size must be large enough to provide an adequate supply of crystals for screening.
- d. Other features are necessary if transient experiments are to be undertaken. These include effective control and regulation of rate of energy and rate of mass input or removal.

We recognize three general types of crystallization; namely, evaporative, cooling, and precipitation. *Evaporative* crystallizations are usually carried out under vacuum and depend on the removal of solvent by evaporation, causing the deposition of solute. Systems exhibiting flat solubility curves are generally handled in this way. *Cooling* crystallizers are those to which is fed a concentrated preheated solution. The crystallizer is cooled by a refrigerant, resulting in solute deposition due to the reduced solubility at the lower crystallizer temperature. Systems exhibiting steep solubility curves can be handled in this way. *Precipitation* crystallizers are those in which supersaturation is generated by adding a third component in which the solute is insoluble or by carrying on a chemical reaction, the product of which is insoluble.

The MSMMPR technique is applicable to all three types of crystallization. However, the latter type is easiest to do on the laboratory scale because it

can be carried out isothermally and at atmospheric pressure. Consequently, problems of heat transfer and pressure control are eliminated. Such precipitation systems are the most convenient for development of laboratory technique and analysis expertise, because fewer uncertainties are inherent in the experiments. Severe problems of removing a representative product sample from a vacuum system are encountered if evaporative crystallization is used.

9.2 Physical Features of the MSMR Crystallizer

In order to achieve the desired degree of mixing with minimum power, a crystallizer with a draft tube should be used. Agitation can be provided with a propeller or a pitched-blade turbine placed concentrically in the draft tube. The draft tube should be of such a diameter and positioned such that the cross section to the flow is uniform throughout the vessel. It is helpful to place vertical vanes in the annular space to reduce the radial motion of the circulating slurry. The flow pattern resulting from this geometry gives a uniform dispersion of the crystal sizes and therefore permits operation at a minimum power input. This is very important if studies intended to determine the effects of agitation and effects of crystal-crystal contact on nucleation rate are to be made. The factors which limit the degree of agitation in order to maintain a uniform suspension are maximum crystal size and relative crystal-mother liquor density.

One would prefer isokinetic withdrawal of the slurry for the reasons previously mentioned; however, it is satisfactory if the sampling and the product withdrawal tube are placed parallel to the circulation flow and withdrawal made in the direction of flow. The withdrawal velocity must reasonably match the circulation velocity at the point of removal and be of such a magnitude that the settling effects due to density differences are minimized. If these criteria are followed, little classification at the outlet is encountered.

One usually operates crystallizers such as these with 15–60-min drawdown times; consequently, for laboratory-size crystallizers, the average outflow is very small—too small to eliminate classification if removed continuously. It is therefore necessary to use intermittent product withdrawal so that high withdrawal velocities can be achieved. This is best done with a liquid-level control device, usually an electrical contact, and a time-delay relay. The relay activates a pump which runs for a predetermined time. The relay selected should permit the pump to remove no more than 10% of the vessel contents. Figure 9.2-1 shows a typical apparatus including the agitator, draft tube, and withdrawal device.

As mentioned before, residence times of 15–60 min are convenient. Steady state is reached in this kind of crystallizer in 10–15 residence times. Normally,

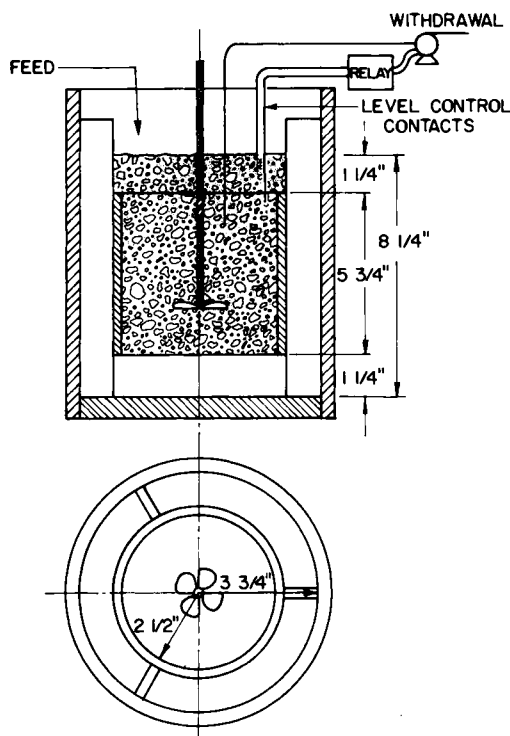


Fig. 9.2-1 Typical MSMPR apparatus with provision for intermittent discharge (apparatus used in Chemical Engineering Department, Iowa State University, Ames, Iowa).

a slurry sample of 500 ml is required to provide a suitable sample for screen analysis. All of these factors suggest a crystallizer of about 10-liter capacity. This would require a total feed supply of about 200 liters for an experiment designed to measure the nucleation and growth rates of crystals. Smaller systems could be used, but care must be taken when sampling so as not to disturb the system, and the sizing of small samples leads to increased sizing error.

EXAMPLE 9.2-1 PRECIPITATION CRYSTALLIZER

The crystallizer shown in Fig. 9.2-1 was used by the author [1] for a number of experiments designed to test the analysis and to determine the kinetics of nucleation and growth for a number of compounds in the presence of water and alcohol. The crystallizer was a 5½-liter Plexiglas vessel with a Plexiglas

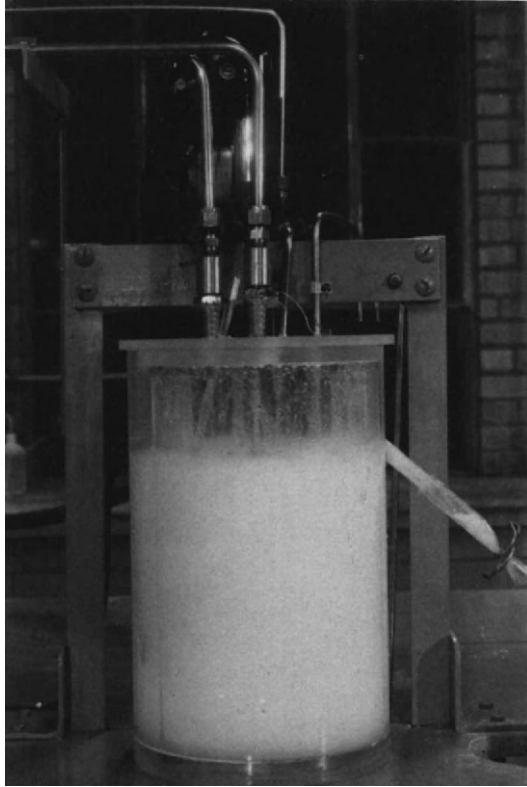


Fig. 9.2-2 Precipitation crystallizer with dimensions of that in Fig. 9.2-1 (apparatus used in Chemical Engineering Department, Iowa State University, Ames, Iowa).

draft tube fixed in place with three vertical vanes in the annular space. The dimensions are as shown in Fig. 9.2-2. A Lightning model V5 mixer was used to provide agitation and was operated at maximum speed. Alcohol was gravity-fed through a constant-head tank, as was the feed solution. The addition of the alcohol created the supersaturated condition which resulted in crystallization.

The product removal was accomplished by using a relay with a contact in the solution and one directly above the solution. Product removal was achieved when the liquid surface came in contact with the electrode above the surface. This actuated a rotary pump which was operated through a time-delay relay. The delay relay operated the pump for the time required to remove 10% of the vessel contents. ♦

EXAMPLE 9.2-2 COOLING CRYSTALLIZER

The crystallizer shown in Fig. 9.2-3 was used to determine the kinetics of several potassium compounds by cooling crystallization [2]. It was also used to determine the effects of temperature and additives on the nucleation kinetics. The crystallizer consisted of a 10.5-liter vessel constructed of Panelcoil. A draft tube was similarly constructed of Panelcoil and both the vessel wall and the tube were cooled by circulating refrigerated ethylene glycol through the tubes. Agitation was provided by a Lightning model V5 mixer. Product removal was accomplished in the same way as described in Example 9.2-1. The feed was contained in electrically heated drums and was filtered just prior to entry into the crystallizer by a line filter. ♦

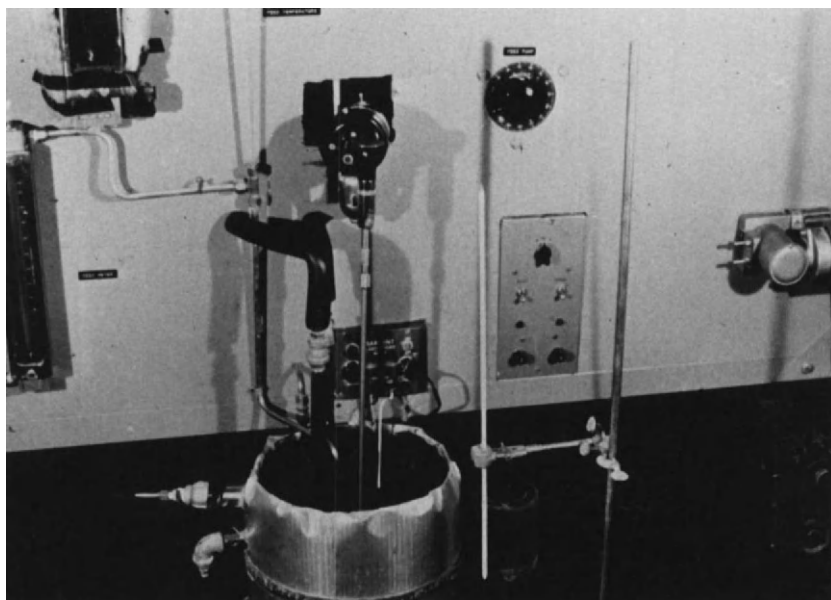


Fig. 9.2-3 Cooling crystallizer (apparatus used in Chemical Engineering Department, Iowa State University, Ames, Iowa).

EXAMPLE 9.2-3 EVAPORATIVE CRYSTALLIZER

The vacuum crystallizer shown in Fig. 9.2-4 was used in work on the evaporative crystallization of potassium sulfate [3]. Dimensions are as shown in the figure. No draft tube was used but mixing was achieved by baffling. The vessel was an eight-liter Pyrex glass cylinder closed on either end by brass

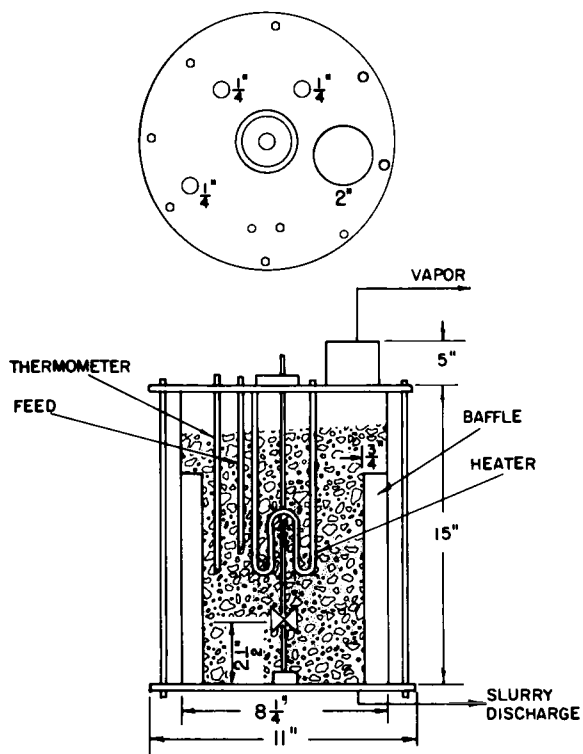


Fig. 9.2-4 Evaporative crystallizer [H. N. Rosen, and H. M. Hulburt, *Chem. Eng. Progr. Symp. Ser. 110* 67, 18 (1971)].

plates. The agitator operated at 1000 rpm for all experiments. The product was removed at intervals from the bottom through a vacuum removal system. ♦

EXAMPLE 9.2-4 PRECIPITATION CRYSTALLIZATION

The crystallizer shown in Fig. 9.2-5 was used by Bransom *et al.* [4] in the crystallization of cyclonite. This work constituted the first reported use of the MSMPR crystallizer to obtain quantitative nucleation–growth rate kinetics. ♦

EXAMPLE 9.2-5 COOLING-PRECIPITATION CRYSTALLIZER

Figure 9.2-6 gives the schematic flow diagram [5] for the combination cooling–precipitation crystallizer shown in Fig. 4.2-1. Cooling and/or precipitation can be used in this apparatus to provide the driving forces for

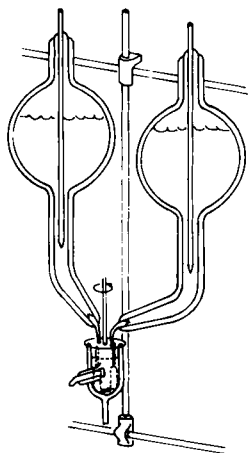


Fig. 9.2-5 Precipitation crystallizer for crystallization of cyclonite [after S. H. Bransom, W. J. Dunning, and B. Millard, *Discuss. Faraday Soc.* **5** 83 (1949)].

crystallization. The suspension holdup in this crystallizer is approximately two liters, which represents essentially the lower limit on size for such MSMR units. Reduction in scale was achieved by winding the cooling coil in a tight spiral to serve as a draft tube. Small amounts of product discharge (~ 100 cc) were removed for size analysis using a Coulter counter. Such units can be automated to operate several shifts (for example, overnight) without operator attention. It should be noted that total run time to achieve steady-state CSD is a function of the retention time τ and not the size scale of the apparatus. ♦

In addition to the basic vessel and the discharge technique, the apparatus must include appropriate feed tanks and metering and control devices, as well as in-line microfilters for filtering the feed. Care must be taken so that no crystallization takes place before the feed enters the crystallizer.

In the case of a precipitation system, two feed tanks and two feed streams are required. These streams should be introduced at the point of greatest agitation, namely in the draft tube, with the flow in the draft tube downward. When transient runs are made which involve changes in the relative flow rates of the two streams, the effect of change in residence time must be accounted for.

Cooling crystallizers may be constructed of plastic, glass, or stainless steel and may be cooled by brines or suitable organic coolants. In any event, the surface area for cooling should be large, the temperature difference between the coolant and the mother liquor should be small, and the cooling surface should be smooth and polished. All of these factors will help reduce crystal buildup on the surface of the draft tube or the vessel walls.

Transient experiments with cooling crystallizers are very difficult to make because they generally require changes in flow rates. This requires com-

mensurate changes in rate of heat transfer. Such requirements need to be carefully examined to see that the heat balances are satisfied.

In cooling systems, crystallized material may be conserved by recycling the product to a redissolving tank and recycling it to the crystallizer. If this is done over long periods, care must be taken to ensure that evaporation does not take place, that no crystals remain undissolved in the feed drum, and that extraneous impurities (e.g., corrosion products) do not build up in the feed.

Laboratory-size, continuous evaporative crystallizers are much more difficult to operate because they are usually under vacuum. This causes difficulty in designing an acceptable withdrawal system, as vacuum operation can cause vapor-lock.

9.3. Measurement of Size Distribution

The validity of the kinetic measurements depends upon achieving the conditions assumed in the derivation of the size distribution representation

$$n = n^0 \exp(-L/G\tau) \quad (9.3-1)$$

However, even if the crystallizer conditions are met, the sampling procedures and sample treatment can destroy the validity of the results.

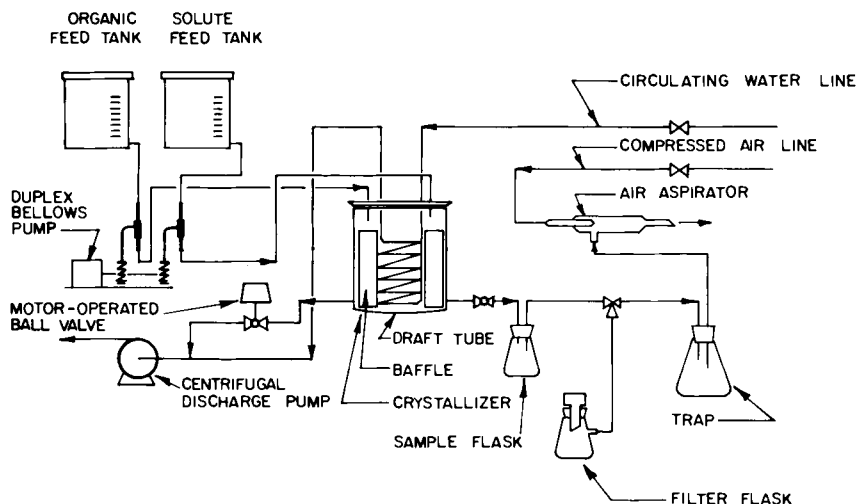


Fig. 9.2-6 Schematic flow diagram of bench-scale cooling precipitation crystallizer [R. Crawford, M. S. Thesis, Univ. of Arizona, Tucson, Arizona, 1969, unpublished].

As previously mentioned, a representative slurry sample must be removed rapidly and carefully so that crystals are not fractured and so that continued crystallization does not take place. Because of the relatively low supersaturation existent in most backmixed systems, continued crystallization after withdrawal is not a problem if the temperature is maintained precisely.

The greatest difficulty lies in the separation of the crystals from the mother liquor. Care must be taken to assure that all crystals are removed from the mother liquor and, once "dewatered," that agglomeration does not occur.

The sample should be removed via a vacuum bottle and calibrated flask so that the exact volume of slurry can be determined. As discussed in Chapter 3, population densities can be reported on either a slurry or mother liquor basis. In the latter case, the volume of clear liquor filtrate is measured. The bottle should be the same temperature as the slurry. The sample probes in the vessel should be placed similarly to that specified for the continuous withdrawal. A micropore, Buchner-type vacuum filter works well for aqueous inorganic systems. The greatest difficulty is in washing and drying the crystals. Usually, the experimenter must develop his own technique but a good way to start is to add a suitable organic solvent in which the crystals are not soluble immediately after dewatering. The crystals should then be stirred and the solvent drawn off through the filter. After two or three such washes, the crystals will have little tendency to agglomerate. Suitable solvents for inorganics are acetone, light alcohols, light ketones, or light aldehydes. The samples should be carefully removed from the filter, spread on a water glass, and dried at a temperature well below the crystal decomposition temperature. Special care must be taken for hydrated crystals. Normally, such a procedure results only in very light agglomeration which is broken up upon screening. The authors have used this method extensively and little agglomeration was detected under microscopic examination.

Such representative product crystal samples are normally sized by standard sieving techniques. Three-inch standard screens are useful because of the sample size. Sizes below $100\text{ }\mu\text{m}$ are best examined by a counting device such as a Coulter counter. When this instrument is used, crystals of a rather narrow size fraction must be suspended in an electrolyte for counting. It is sometimes difficult to find an electrolyte in which the crystals are insoluble.

Depending on the method of analysis, the distributions are obtained either as mass distributions or number distributions. The data may be treated in a number of ways to obtain the growth and nucleation rates. Below, we give two methods.

EXAMPLE 9.3-1 USE OF POPULATION DENSITY

- a. If the distribution is obtained by sieving in terms of mass distribution,

the arithmetic average size of each fraction is first determined. If possible, a suitable shape factor for the crystals is determined. If this is not possible, a shape factor of unity can be used to obtain a "relative" population density.

b. A basis must be determined because population density has dimensions numbers/size/basis. A useful basis is the suspension density per unit volume of crystallizer. In order to put the computation on this basis, the mass distribution must be connected to the mass concentration per unit volume of slurry. To do this, the suspension density must be known.

c. With the distribution per unit volume of suspension known, the population density of each size can be determined by

$$(n)_L = (M_T \Delta W) / (\rho k_v \bar{L}^3 \Delta L) \quad (9.3-2)$$

where k_v is the shape factor, $\bar{L}$ the arithmetic average size of crystals in the size range L_1 to L_2 , $\Delta L = L_2 - L_1$, ρ is the absolute density of crystalline species, ΔW is the weight fraction of crystals in the size range L_1 to L_2 , and M_T is the suspension density in the crystallizer magma.

From Eq. (9.3-1), a plot of $\log n$ versus $\bar{L}$ should give a straight line of slope $-1/G\tau$ and intercept n^0 . As discussed previously, the product of growth rate and nuclei density Gn^0 is the nucleation rate B^0 . Data often scatter from the ideal exponential relationship. It is best, therefore, to use a least squares fit with the constraint

$$M_T = 6k_v \rho n^0 (G\tau)^4 \quad (9.3-3)$$

where M_T is the independently measured suspension density. Note that the slope and intercept are both incorporated in Eq. (9.3-3). ♦

EXAMPLE 9.3-2 USE OF THE GAMMA FUNCTION

A simplified and rapid technique, useful for analyzing an entire set of sieve measurements or for estimating growth and nucleation rates from a single point on the cumulative weight–size distribution, exploits the fixed form of the MSMR exponential distribution. Use of this technique to estimate growth and nucleation rates from a single CSD data point will be illustrated.

Cumulative CSD from a MSMR crystallizer is tabulated in Appendix A as the dimensionless $w(x)$ function, where

$$w(x) = \frac{1}{6} \int_0^x \exp(-p) p^3 dp \quad (9.3-4)$$

Assume a data value near the midpoint of the cumulative weight–size distribution curve; for illustration purposes, pick $W(L) = w(x) = 0.5$. Let $\bar{L}_{50}$

represent this median size of the distribution. From Appendix A, the dimensionless median size is given as

$$\bar{x}_{50} = 3.67 \quad (9.3-5)$$

Thus, from the definition of dimensionless size $x = L/G\tau$, the growth rate is calculated as

$$G = \bar{L}_{50} / \bar{x}_{50} \tau \quad (9.3-6)$$

Density of nuclei is obtained from the mass balance equation as

$$n^0 = M_T / 6\rho k_v (G\tau)^4 \quad (9.3-7)$$

The procedure can be repeated for any other size on the cumulative weight-size distribution curve. If the distribution fits the theoretical MSMR form, identical values of G and n^0 will be calculated. Some scatter about the MSMR form is to be expected and the G values can be weight-averaged according to the mass fraction distribution dW/dL at that size. ♦

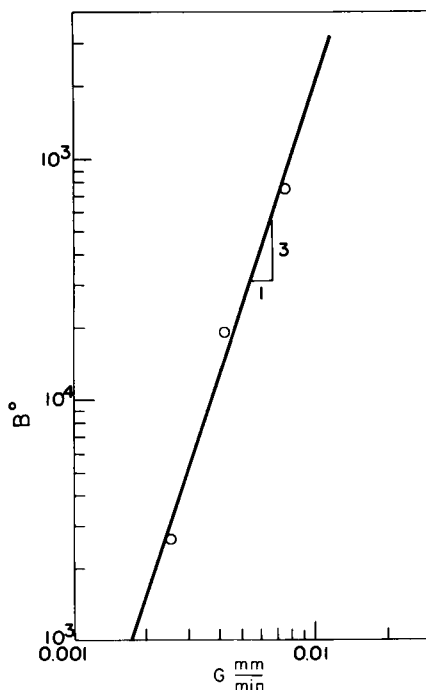


Fig. 9.4-1 Nucleation kinetics of cyclonite [S. H. Bransom, W. J. Dunning, and B. Millard, *Discuss. Faraday Soc.* 5, 83 (1949)].

9.4 Reported Data

A number of investigators have determined kinetic relationships using apparatus of the MSMPR type previously described. These results can usually be correlated satisfactorily in terms of power-law kinetic models. As previously stated, the level of supersaturation in MSMPR crystallizers is very low and often unmeasurable; therefore, the nucleation kinetics are reported in conjunction with, and related to, the growth rates existing at the time of measurement. The level of supersaturation will be included in those cases where it was reported.

The earliest reported work [4] using steady-state mixed suspension crystallization to characterize kinetics was done in 1949, crystallizing cyclonite (RDX) explosive by a precipitation technique from solution in water and nitric acid. Supersaturation data scattered, probably because of analysis problems, but the growth rates were very reproducible, as were the nuclei population densities. Results are shown in Table 9.4-1.

Table 9.4-1
Data on Cyclonite^a

Temperature (°C)	Mother liquor composition (%)	τ (min)	G ($\mu\text{m}/\text{min}$)	Super- saturation	B^0 (number/ml- min $\times 10^{-4}$)
66.5	54.1	2.40	8.6	0.016	8.4
68.5	54.4	2.25	7.7	0.047	9.3
67.5	56.0	2.60	7.6	0.018	7.0
66.7	53.1	3.0	6.4	0.066	7.2
68.8	53.0	2.8	7.9	0.039	6.2
67.8	53.7	2.9	6.9	0.030	7.4
	Average	2.7	7.6	0.043	7.3
66.4	54.7	5.7	5.6	0.044	1.4
65.6	53.0	6.1	4.0	0.020	1.7
65.0	54.6	6.1	3.5	0.020	2.6
	Average	6.0	4.3	0.028	1.9
66.0	52.6	13.5	2.6	0.006	0.28
66.0	53.9	14.5	2.9	0.010	0.20
66.3	53.6	14.5	2.1	0.030	0.30
	Average	14.0	2.5	0.015	0.26

^aS. H. Bransom, W. J. Dunning, and B. Millard, *Discuss. Faraday Soc.* 5, 83 (1949).

The nucleation rate, plotted versus the growth rate in Fig. 9.4-1, gives a line with slope of 3. The proper kinetic expression, then, is

$$B^0 = k_N G^3 \quad (9.4-1)$$

By averaging the supersaturation data, one gets a linear relationship with growth, so that for cyclonite,

$$B^0 = k'_N s^3 \quad (9.4-2)$$

The kinetics of nucleation and growth for the crystallization of ammonium alum [1] by addition of ethyl alcohol to an aqueous solution have been re-

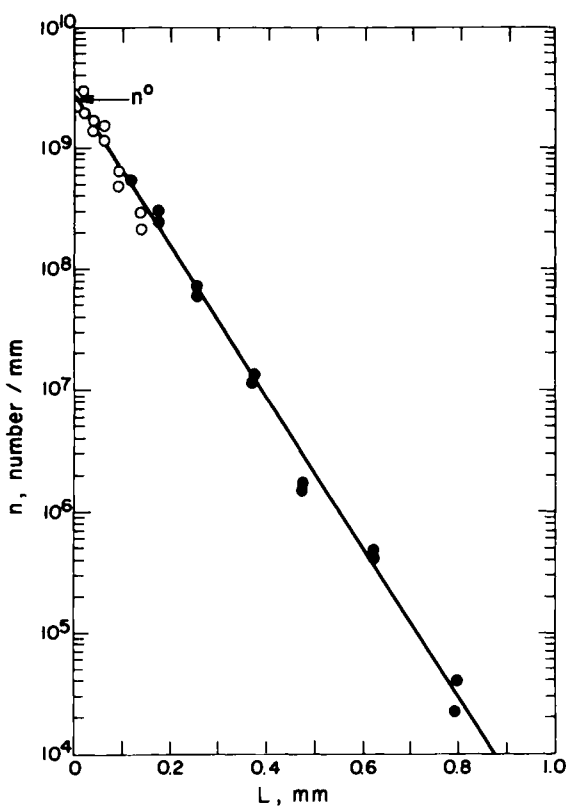


Fig. 9.4-2 CSD of ammonium alum obtained by precipitation with ethyl alcohol. $T = 80^\circ\text{F}$; $M_T = 6.3 \times 10^{-2}$ gm/ml; $\tau = 15$ min; basis, total crystallizer volume ($5\frac{1}{2}$ liters). Sieves (●); Coulter counter (○) [D. C. Timm, and M. A. Larson, *AIChE J.* **14**, 452 (1968)].

ported. In later work [6], the experiments were repeated with different results; however, they took into account secondary nucleation effects. These data on alum along with data taken in similar experiments with the ammonium sulfate–methyl alcohol–water system and the sodium chloride–ethyl alcohol–water system are plotted in Figs. 9.4-2–9.4-4. The extrapolation of the size-distribution plot to zero to obtain the population density of nuclei is justified as indicated by agreement of population densities of very small crystals measured with a Coulter counter. These data are shown on the plots as the open points.

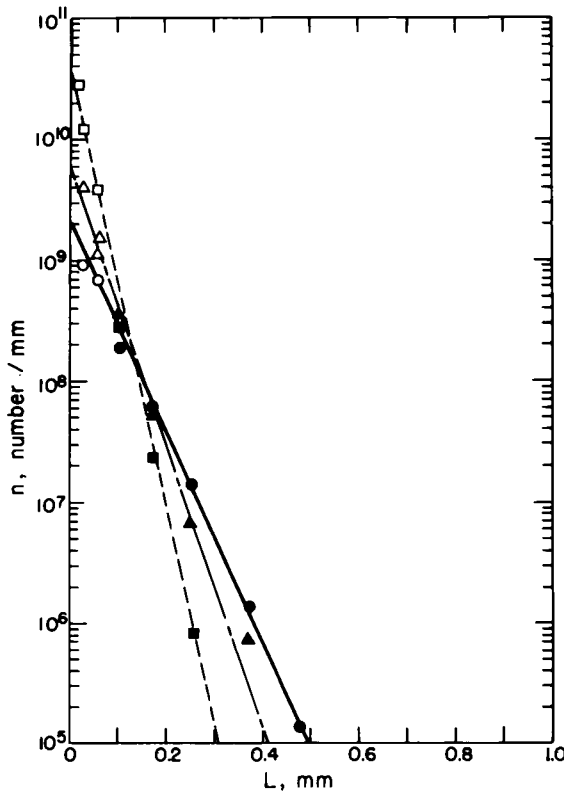


Fig. 9.4-3 CSD of sodium chloride obtained by precipitation with ethyl alcohol. $T = 80^{\circ}\text{F}$; $M_T = 3.3 \times 10^{-2}$ gm/ml; $\tau = 15$ ($\square$), 30 ($\triangle$), 45 ($\circ$) min; basis, total crystallizer volume ($5\frac{1}{2}$ liters). Sieves ($\bullet$); Coulter counter ($\circ$) [D. C. Timm, and M. A. Larson, *AIChE J.* **14**, 452 (1968)].

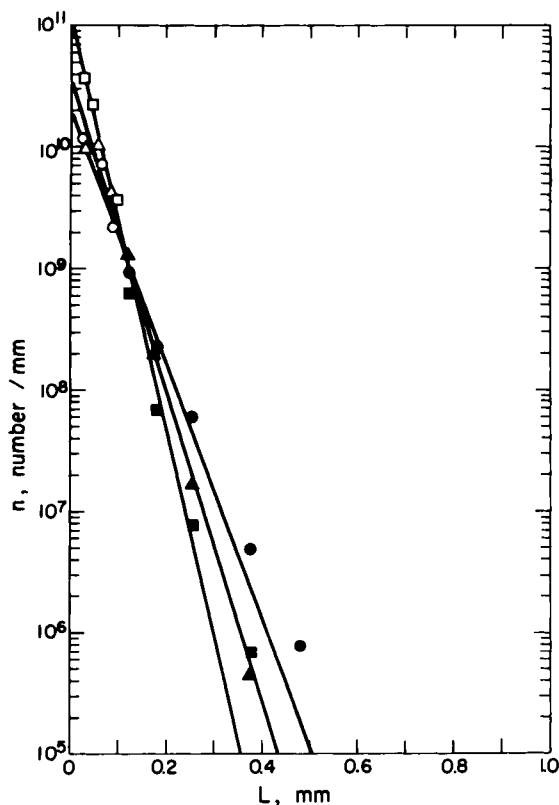


Fig. 9.4-4 CSD of ammonium sulfate obtained by precipitation with methyl alcohol. $T = 80^{\circ}\text{F}$; $M_r = 0.1$ gm/ml; $\tau = 15$ ($\square$), 30 (Δ), 45 ($\circ$) min; basis, total crystallizer volume ($5\frac{1}{2}$ liters). Sieves ($\bullet$); Coulter counter ($\circ$) [D. C. Timm, and M. A. Larson, *AIChE J.* 14, 452 (1968)].

Figure 9.4-5 shows the kinetic correlation of these data. The apparent orders of nucleation for these systems are respectively one, four, and nine for alum, ammonium sulfate, and sodium chloride. It should be recognized that these kinetic orders are not necessarily applicable for crystallization carried out using different techniques, e.g., cooling.

Subsequent work [7] examined the secondary nucleation effects of these systems and found that in all three cases the nucleation rate was linearly dependent on the suspension density.

Figure 9.4-6 shows the size distribution of crystals produced at two levels of suspension density. Parallel lines indicate a linear dependence of nucleation on suspension density.

Work on the production of phosphoric acid via the wet process [8] showed that the relative nucleation-growth rate kinetics of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ from a solution of phosphoric acid and monocalcium phosphate by addition of sulfuric acid is of order 2.6. The temperature of operation was 70°C and the suspension density was 3.7%. This work also indicated that under high-viscosity conditions and low suspension density the effects of secondary nucleation were reduced.

Industrially useful data can often be taken from experiments where crystallization is accomplished by cooling the solution below its saturation level. In these instances, conditions of mother liquor density, viscosity, and surface tension closely approximate those in practical industrial processes.

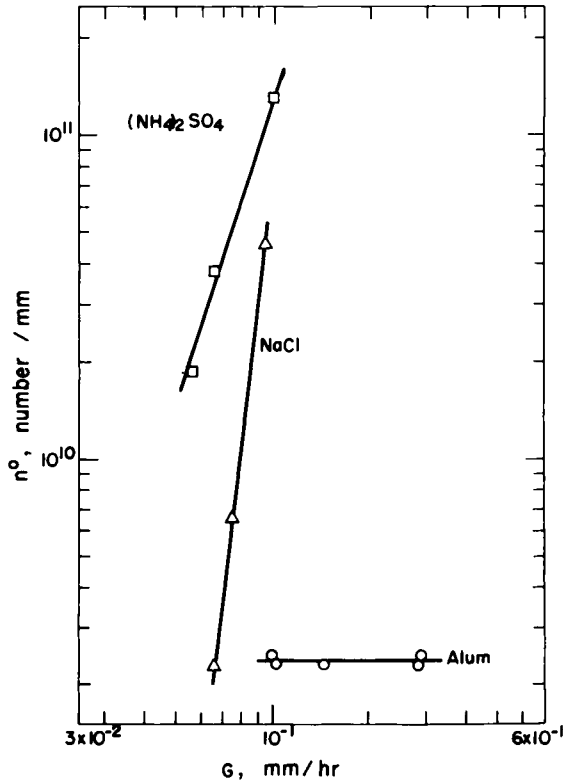


Fig. 9.4-5 Kinetic correlations for ammonium alum (slope = 0, $i = 1$), ammonium sulfate (slope = 3, $i = 4$), and sodium chloride (slope = 8, $i = 9$). $B^0 = KM^i r^i$. Basis: total crystallizer volume ($5\frac{1}{2}$ liters) [D. C. Timm, and M. A. Larson, *AIChE J.* 14, 452 (1968)].

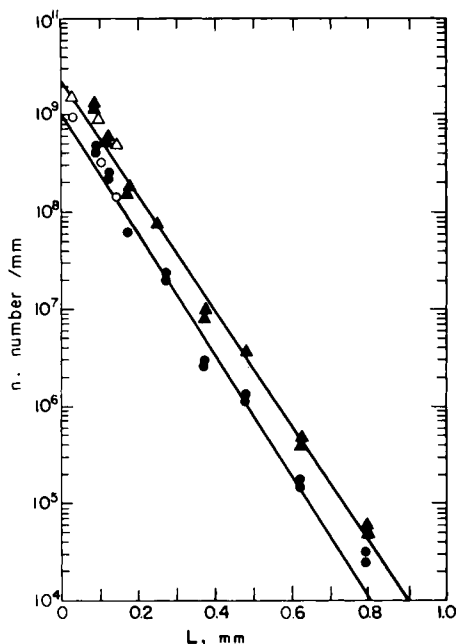


Fig. 9.4-6 Effect of suspension density on CSD. System, alum- H_2O -EtOH; $T = 80^\circ\text{F}$; $\tau = 15$ min; suspension density, ($\circ$ and $\bullet$) 2.0 and (Δ and $\blacktriangle$) 5.4 gm/100 ml; sieves ($\bullet$ and $\blacktriangle$); Coulter counter ($\circ$ and Δ). Basis: total crystallizer volume ($5\frac{1}{2}$ liters) [M. A. Larson, D. C. Timm, and P. R. Wolff, *AIChE J.* 14, 448 (1968)].

Unpublished work by the author and co-workers [9] on the ammonium alum and ammonium sulfate systems by cooling in a well-stirred 11-liter vessel confirmed the extrapolation of the size distribution to zero size by using the Coulter counter for sizing the small sizes. Figure 9.4-7 shows a typical size distribution obtained from these experiments. The order of nucleation for ammonium alum under these conditions was found to be $i = 2$ determined at various suspension densities. The order for ammonium sulfate was $i = 1.5$ over a wide range of suspension densities. A typical plot of this correlation is shown in Fig. 9.4-8. The order with respect to suspension density or suspension area at a given growth rate was 1.0 for both materials.

Several systems [10] were examined to determine the effect of temperature on nucleation-growth rate kinetics; namely, potassium nitrate, potassium chloride, and potassium sulfate. Secondary effects were not examined in this work and the data reflect experimental conditions giving a suspension density of ~ 3 gm/100 ml. The data for the nitrate and chloride are given in Tables 9.4-2 and 9.4-3, respectively.

Table 9.4-2

Experimental Operating Conditions and Results for Potassium Nitrate^a

T (°C)	τ (min)	$C_{i,v}$	$C_{o,v}$	C_s	M_T (gm/100 ml)	$G \times 10^3$ (mm/min)	$n^0 \times 10^{-7}$ (number/mm)	$B^0 \times 10^{-5}$ (number/min)
11.0	15	25.77	21.98	21.76	3.00	6.37	15.80	10.00
11.0	30	26.26	21.78	21.76	3.60	3.92	12.30	4.81
11.0	45	25.70	21.73	21.76	3.07	2.66	11.50	3.06
20.8	15	38.34	32.52	31.98	4.56	7.40	11.60	8.57
20.8	30	38.30	32.50	31.98	3.75	4.23	9.06	3.83
20.8	45	38.70	31.85	31.98	3.77	2.90	8.20	2.37
31.0	15	49.92	46.25	46.48	2.45	8.54	8.79	7.50
31.0	30	52.20	45.88	46.48	3.20	4.55	7.32	3.33
31.0	45	51.70	45.80	46.48	3.25	3.13	6.50	2.03
40.0	15	65.75	62.40	62.34	3.09	9.37	6.26	5.86
40.0	30	65.48	62.50	62.34	2.82	4.86	5.25	2.55
40.0	45	67.05	62.30	62.34	4.13	3.35	4.59	1.53

^a W. J. Genck and M. A. Larson, Joint Meeting AIChE and IMIQ, 3rd, Denver, Colorado, September, 1970, Paper 39e. Here, the vessel volume is 10.5 liters; $C_{i,v}$, $C_{o,v}$, and C_s indicate grams potassium nitrate/100 gm H₂O. n^0 is corrected for all runs to a suspension density of $M_T = 3.00$ gm/100 ml. Consequently, the population density of nuclei and the nucleation rate are actually based on 3.00 gm of suspension, in keeping with the assumption of secondary nucleation.

Table 9.4-3*Experimental Operating Conditions and Results for Potassium Chloride^a*

T (°C)	τ (min)	$C_{i,v}$	$C_{o,v}$	C_s	M_T (gm/100 ml)	$G \times 10^3$ (mm/min)	$n^0 \times 10^{-6}$ (number/mm)	$B^0 \times 10^{-4}$ (number/min)
12.0	15	35.07	32.10	31.98	2.49	12.40	13.80	17.30
12.0	30	34.33	31.98	31.98	2.09	7.55	6.38	4.82
20.8	15	36.89	34.42	34.47	1.98	11.90	18.40	20.30
20.8	30	36.48	34.47	34.47	1.38	7.34	7.80	5.22
30.0	15	39.25	37.18	36.86	1.68	11.30	20.50	23.00
30.0	30	39.75	37.16	36.86	2.07	6.99	10.30	7.21

^a W. J. Genck and M. A. Larson, Joint Meeting AIChE and IMIQ, 3rd Denver, Colorado, September, 1970, Paper 39e. Here vessel volume equals 10.5 liters; $C_{i,v}$, $C_{o,v}$, and C_s indicate grams potassium chloride/100 gm H₂O. n^0 is corrected for all runs to a suspension density of $M_T=2.00$ gm/100 ml.

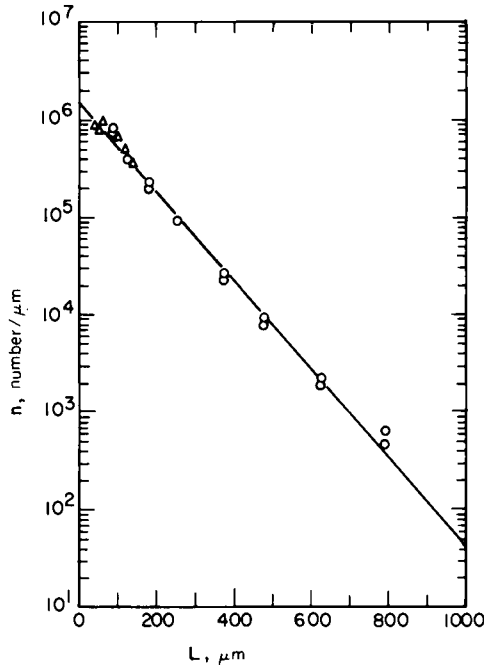


Fig. 9.4-7 CSD of ammonium alum crystallized by cooling. $\tau = 45$ min, $V = 11$ liters, $M_T = 5.3$ gm/100ml, $T = 22^\circ\text{C}$; Coulter counter (Δ); sieve ($\circ$); basis, total crystallizer volume [C. W. Chambliss, Nucleation and growth kinetics in a cooling crystallizer, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1966, unpublished].

No temperature dependence was observed on the order of nucleation over the temperature range covered for either system, although relative nucleation rates increased with temperature for KCl but decreased with temperature for KNO_3 . The order of nucleation for KNO_3 was 1.3 and for KCl was 2.6.

Potassium sulfate has several anomalous characteristics which have been found by many investigators. Growth rates exhibit a definite size dependence, increasing with size and thus resulting in a curved population density plot. Figure 9.4-9 is a typical example of a curved population density plot resulting from increased growth rates at the larger particle sizes. MSMPR data indicate the potassium sulfate system exhibits a small or perhaps negative power-law relationship with growth. Such anomalous nucleation behavior results in a smaller product with longer holding times in an MSMPR crystallizer and undoubtedly results from as-yet-unidentified mechanisms of secondary nucleation.

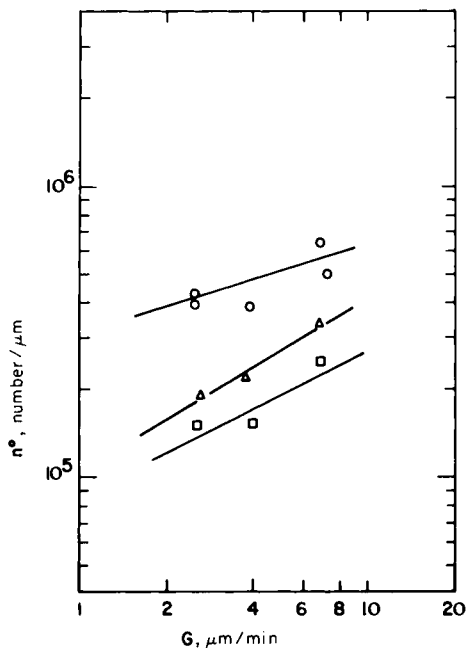


Fig. 9.4-8 Kinetic correlation for ammonium sulfate crystallized by cooling. $\tau = 22^\circ\text{C}$; $M_T = 7.5$ ($\circ$), 4.0 (Δ), 3.0 ($\square$); slope = $i - 1$; basis, total crystallizer volume (11 liters) [C. W. Chambliss, Nucleation and growth kinetics in a cooling crystallizer, Ph.D. Thesis, Iowa State Univ., Ames, Iowa, 1966, unpublished].

Data from evaporative crystallizations are scarce because of experimental difficulties in obtaining the measurements, particularly the difficulty of removing a small, intermittent, but representative, slurry sample. Two investigations have reported kinetic data for nucleation and growth from vacuum systems, one a batch and one a continuous system.

Size distributions of potassium sulfate crystals obtained from a continuous evaporative crystallizer were reported [3]. The crystallizer had a volume of eight liters and a residence time of from 0.31 to 1.47 hr. The supersaturation was measured as well as the size distribution. The growth rate was found to be a function of the square of supersaturation, with the nucleation rate a linear function of the suspension density but not a function of supersaturation. Such supersaturation-independent nucleation rates indicate a value of zero for the nucleation sensitivity parameter i .

A typical size distribution from these experiments is shown in Fig. 9.4-10. Note that the change in slope suggests size-dependent growth, although this

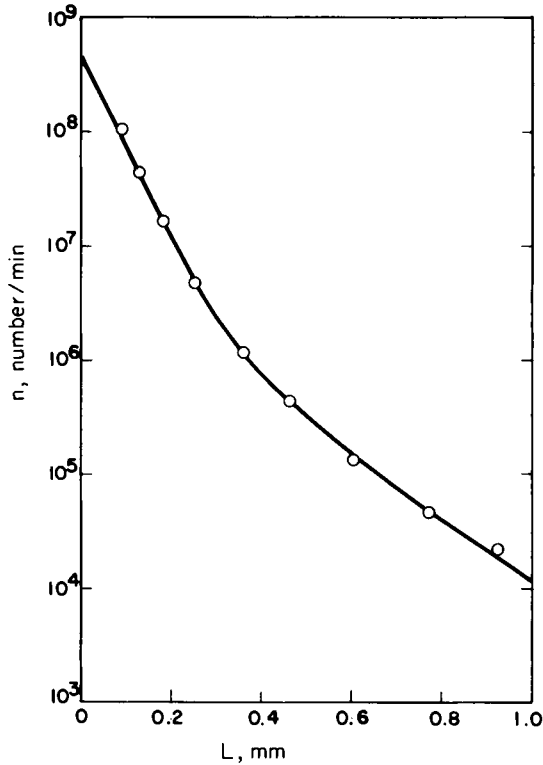


Fig. 9.4-9 CSD of potassium sulfate crystallized in a laboratory crystallizer by cooling. $T = 30^\circ\text{C}$; basis, 100 ml slurry [W. J. Genck, Temperature effects on growth and nucleation rates in mixed suspension crystallization, Ph.D. Thesis, Iowa State Univ. Ames, Iowa, 1969, unpublished].

effect was not taken into account in data analysis. These results are not inconsistent with the results from a continuous cooling crystallizer discussed above.

The anomalous results of various investigations on the K_2SO_4 system indicate that this is a very unusual crystal system. Further detailed study seems warranted to conclusively identify the secondary nucleation mechanisms.

9.5 Crystallization with Additives

Trace chemical additives are often used to suppress or promote nucleation and/or promote better crystal growth and habit. Such additives are often considered proprietary information by industrial companies and hence few

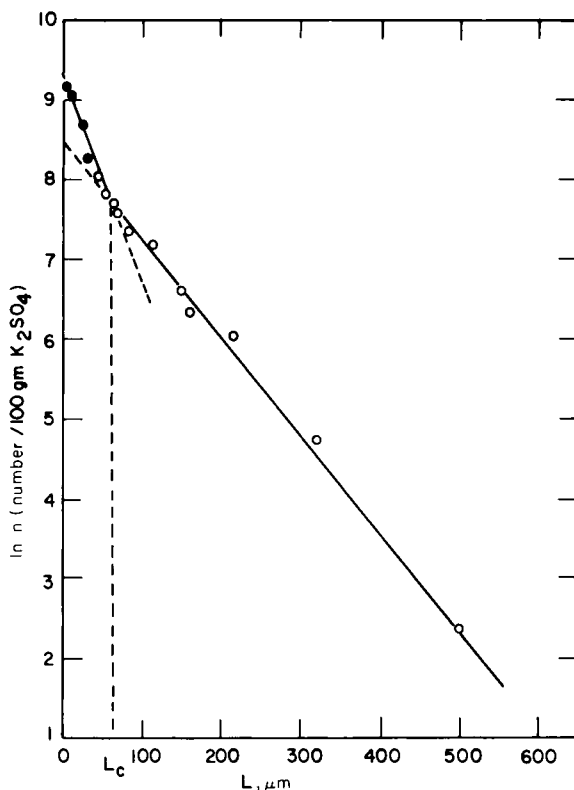


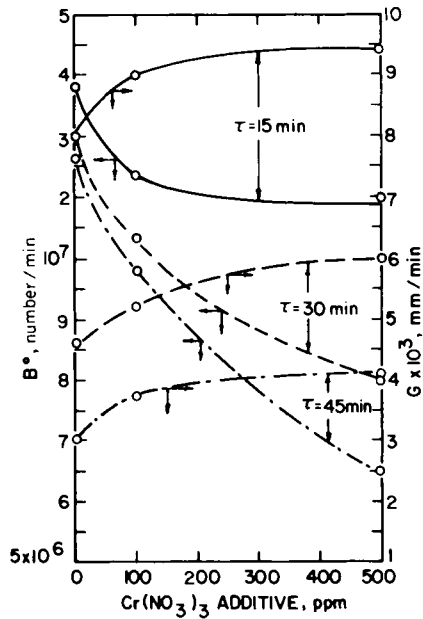
Fig. 9.4-10 CSD of potassium sulfate crystallized in a laboratory crystallizer by evaporation. $S = 0.41$ gm $K_2SO_4/100$ gm H_2O ; $\tau = 0.808$ hr; $T = 30.0^\circ C$; sieve ($\circ$); coulter counter ($\bullet$) [H. N. Rosen, and H. M. Hulburt, *Chem. Eng. Progr. Symp. Ser. 110* 67, 18 (1971)].

published data exist on this subject. Practically no quantitative data have been published on the effects of additives on nucleation kinetics; however the effects of various soluble additives on the size distribution of KNO_3 crystals have been reported [2]. It was assumed that secondary nucleation was the primary source of nuclei and that the additives affected the surface condition of crystals in suspension and consequently the nucleation rate.

The results from experiments using $Cr(NO_3)_3$ as an ionic additive are plotted in Fig. 9.5-1 as a function of $Cr(NO_3)_3$ concentration. Note that the nucleation rate decreases and the growth rate increases as the additive concentration increases. This is consistent with the view that large, highly charged anions block nucleation sites on the surface of the crystal. Somewhat surprising, however, is the observation that in the presence of these anions, the relative order of nucleation i is increased from 1.8 to 2.4.

Three surface-active agents, methylamine hydrochloride, dodecylamine hydrochloride, and a fluorocarbon (FC-98, 3M Company) were also used and the results are shown in Figs. 9.5-2 and 9.5-3. These plots show that nucleation rate increases with surfactant concentrations and the growth rate decreases. One notes that there seems to be a maximum. This is analogous to the adsorption isotherms found in other systems and suggests that the surface-active agent is adsorbed on the surface. No generality should be attached to

Fig. 9.5-1 Nucleation and growth rates for KNO_3 in the presence of $\text{Cr}(\text{NO}_3)_3$; basis 1 gm KNO_3 [S. M. Shor, and M. A. Larson, *Chem. Eng. Progr. Symp. Ser. 110* 67, 32 (1971)].



these results, however. Additives are usually quite specific in their effect on nucleation and surface-active agents are known to inhibit, rather than accelerate, nucleation in many other systems.

Again, for the KNO_3 system, the order of nucleation was increased in the presence of surfactant but was unaffected by the concentration of additives. The order was increased from 1.8 to 2.5 in all cases.

A similar investigation by Liu and Botsaris [11] has shown the effect of lead ion on the size distribution of sodium chloride. These experiments were conducted with a precipitation crystallizer similar to that of Timm and Larson [6], using ethyl alcohol to precipitate sodium chloride. The crystallization was carried out in the presence of various concentrations of PbCl_2 . The results are shown in Fig. 9.5-4. As lead ion concentration increases, the

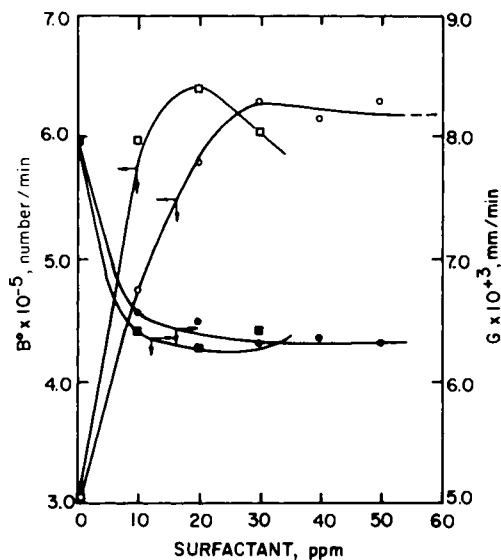


Fig. 9.5-2 Nucleation and growth rates for KNO_3 in the presence of surface-active agents. Squares: fluorocarbon FC-98 (3M Company); circles: $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\text{HCl}$; Basis: 1 gm KNO_3 ; $\tau = 15$ min [S. M. Shor, and M. A. Larson, *Chem. Eng. Progr. Symp. Ser. 110* 67, 32 (1971)].

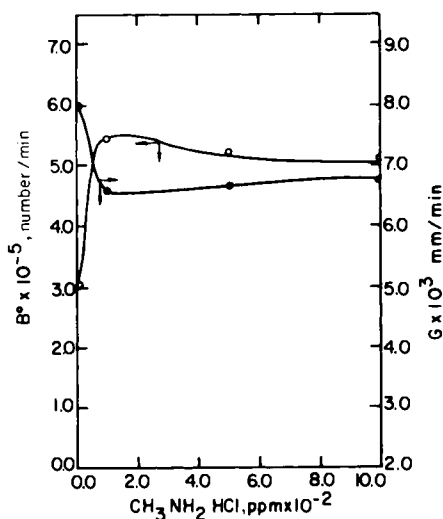


Fig. 9.5-3 Nucleation and growth rate for KNO_3 in the presence of methylamine hydrochloride; basis: 1 gm KNO_3 ; $\tau = 15$ min [S. M. Shor, and M. A. Larson, *Chem. Eng. Progr. Symp. Ser. 110* 67, 32 (1971)].

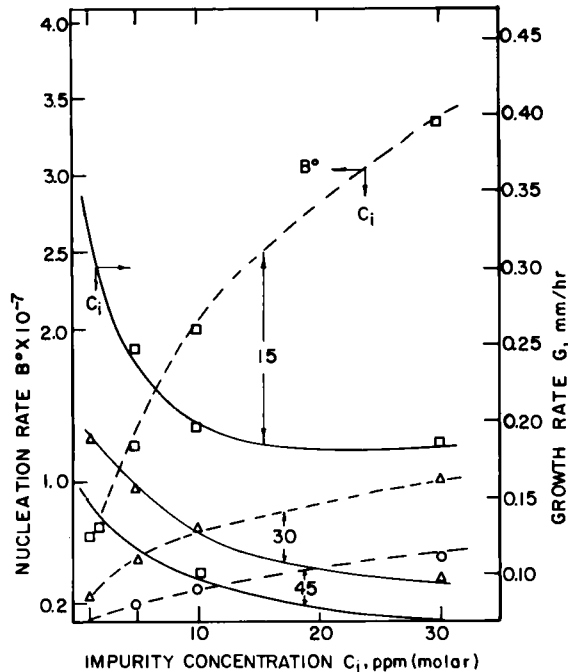


Fig. 9.5-4 Nucleation and growth of NaCl in the presence of ethyl alcohol and PbCl_2 ; $\tau = 15$ ($\square$); 30 (Δ); 45 ($\circ$) min [after Y. A. Lui and G. D. Botsaris, Annual Meeting AIChE, 63rd, Chicago, Illinois, 1970, Preprint 18C].

growth rate decreases and the nucleation rate increases. This effect is just the opposite of the effects of Co^{++} and Cr^{+3} found by Shor and Larson in the crystallization of KNO_3 by cooling. The nucleation order i was found to be 2.25 and was unaffected by the concentration of lead ion. The order was considerably lower than that found by Timm and Larson in experiments in the absence of lead impurity.

These differences might be explained on two counts. In this work, two impurities were present, namely an organic one, ethyl alcohol, and an inorganic one, lead ion. It was also observed that lead was incorporated in the sodium chloride crystals. This was not the case for cobalt and chromium in the potassium nitrate crystallizations. It is possible the lead ion produced a large reduction in the kinetic growth rate constant, thus changing the relative ease of growth to nucleation. In order to achieve the same rate of make at a given throughput, this reduction in the growth rate constant would necessarily cause an increase in supersaturation, causing a high nucleation rate. Alternately, these data could be explained by an increase in the nucleation rate

constant; only measurement of the homogeneous driving forces (supersaturation) could delineate the basic kinetic factors which were altered.

In any event, it is clear from the above two examples that it is dangerous to generalize on the effects of foreign soluble material on nucleation and growth kinetics, as only the relative values of these kinetics affect CSD. In order to clearly determine the effects of impurities on kinetics, it is necessary to measure supersaturation precisely during the crystallization experiment so that the independent effects of the impurities on nucleation and growth can be separated. The MSMR crystallizer provides a powerful means for measuring growth and nucleation simultaneously; measurement of supersaturation along with these kinetic measurements will contribute greatly to the understanding of the effects of impurities.

9.6 Automatic Particle Counting in a Continuous Mixed System

The MSMR crystallizer represents a valuable tool for the study of secondary nucleation and growth rate kinetics in realistic crystallization environments. However, it is of little value in discriminating the specific mechanisms of secondary nucleation, although the presence of secondary factors can be established and correlated. For example, secondary nucleation mechanisms depend in some way on the CSD existing in a mixed magma, say a function of crystal surface, mass concentration, or of the higher moments. Yet, the distribution of crystal sizes, and hence all moments of the distribution, is itself a dependent variable resulting from the crystallization kinetics (secondary) and other crystallization conditions. Typically, nucleation data correlate with the third moment (solids concentration) but they also correlate with the second or higher moments. The moments themselves are interrelated with the steady-state MSMR distribution as

$$m_j = jG\tau m_{j-1} \quad (9.6-1)$$

and thus are highly autocorrelated. However, if power-law correlations of secondary nucleation with G and m_3 also require powers of the retention time τ (not a state variable) to adequately represent the data, then moments other than m_3 represent the particular secondary effects. The dependence on τ can be eliminated and the correct correlating moment identified by substitution of Eq. (9.6-1). True discrimination of secondary mechanisms in a mixed crystal magma demands experimental conditions where the CSD comprising the secondary nucleation environment is a truly independent variable.

Figure 9.6-1 is a photograph of an experimental apparatus [12, 13] which can discriminate nucleation mechanisms while yielding useful kinetic data in

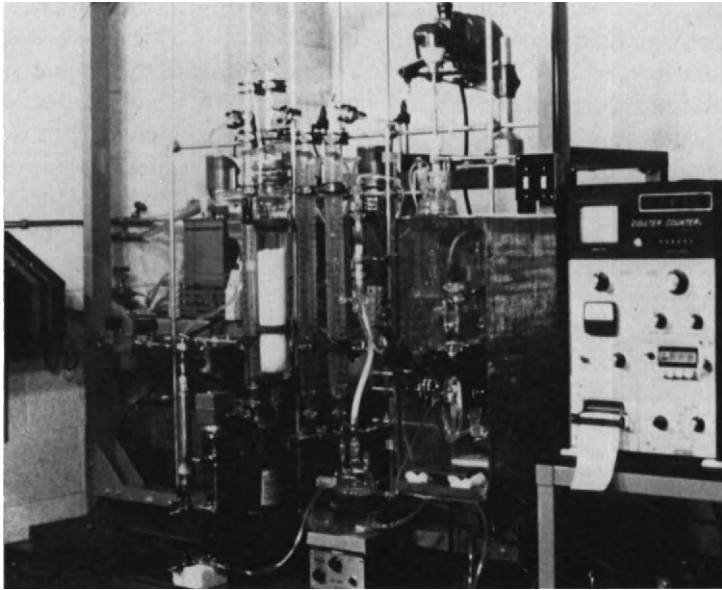


Fig. 9.6-1 Nucleation-growth rate apparatus utilizing multi channel electronic particle counter for *in situ* particle measurement (Chemical Engineering Department, University of Arizona, Tucson, Arizona).

a realistic mixed magma crystallization environment. The apparatus consists of a circulating loop of mother liquor which is brought to saturation in a bed packed with solute crystals together with a small, mixed suspension vessel in which the circulating liquor is backmixed to a controlled, and small, degree of subcooling. Overflow from the mixed crystallizer recirculates through the packed bed. A detailed process flow diagram for this apparatus is shown in Fig. 9.6-2. Secondary nucleation occurs in the mixed vessel upon introduction of an *arbitrary* distribution (size and mass) of seed crystals. This arbitrary secondary nucleation environment is retained in the vessel by a fine stainless steel screen over the outlet (150 or 200 mesh screen) through which passes the fines developed by secondary nucleation. This fine-crystal distribution is measured by on-line counting of particles in the 2–40- μm size range using a multichannel particle size analyzer (Coulter model “T”). Salient features of this apparatus and technique are listed below :

- a. Retention times of 6–10 min in the mixed vessel are used, guaranteeing rapid decay and quasisteady-state adjustment of the fine-crystal distribution.
- b. Conditions of supersaturation and retained CSD in the mixed vessel are representative of the secondary nucleation environment in industrial crystallizers with much longer retention times.

c. The secondary environment (seed crystal CSD) slowly changes with time due to growth. Fine-crystal population may reach a quasisteady state at each state of the secondary environment, but in general, fine-crystal population measurements must be analyzed with the dynamic form of the population balance.

d. The retaining screen is kept from possible plugging by a frequent, periodic hydraulic backflush.

e. Total recycle of mass is obtained in the circulating liquor; thus, cooling and total condensation evaporation, but not salting modes of supersaturation generation, are permissible.

f. The circulating conductive mother liquor induces stray currents in the particle counter; to reduce this noise, the outside electrode is kept at ground potential.

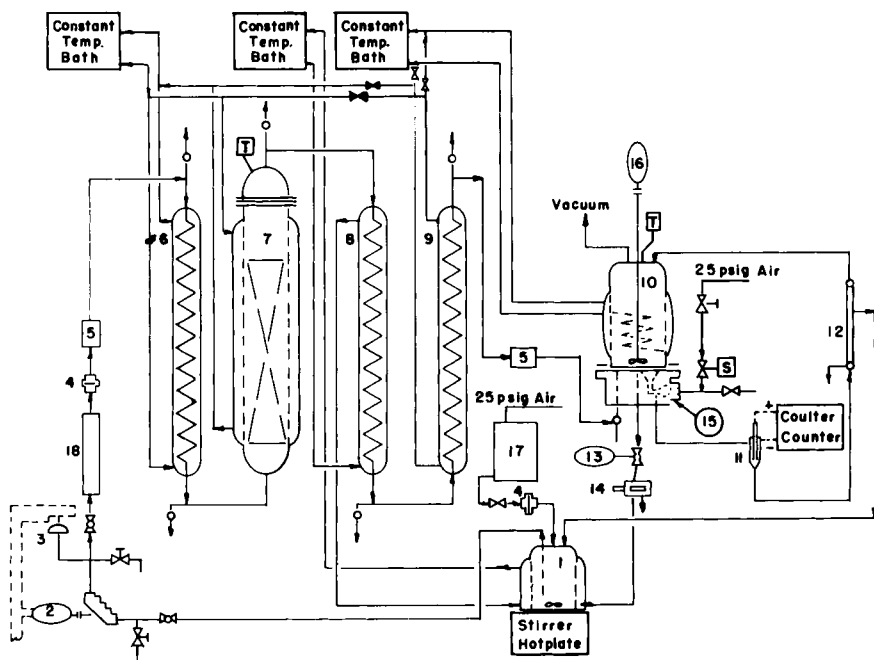


Fig. 9.6-2 Schematic process flow of nucleation-growth rate apparatus shown in Fig. 9.6-1. (1) Surge tank, (2) metering pump, (3) pump pressure switch, (4) disk filter, (5) pall filter, (6) preheater, (7) saturator, (8) sterilizer, (9) pre-cooler, (10) crystallizer, (11) counter sampling cell, (12) volume control tube, (13) crystal drawdown valve, (14) sampling slide valve, (15) back-flush diaphragm, (16) variable-speed stirrer, (17) solution supply tank, (18) activated charcoal bed [M. D. Cise, and A. D. Randolph, Joint Meeting AIChE and IMIQ, 3rd, Denver, Colorado, 1970, Paper 39d].

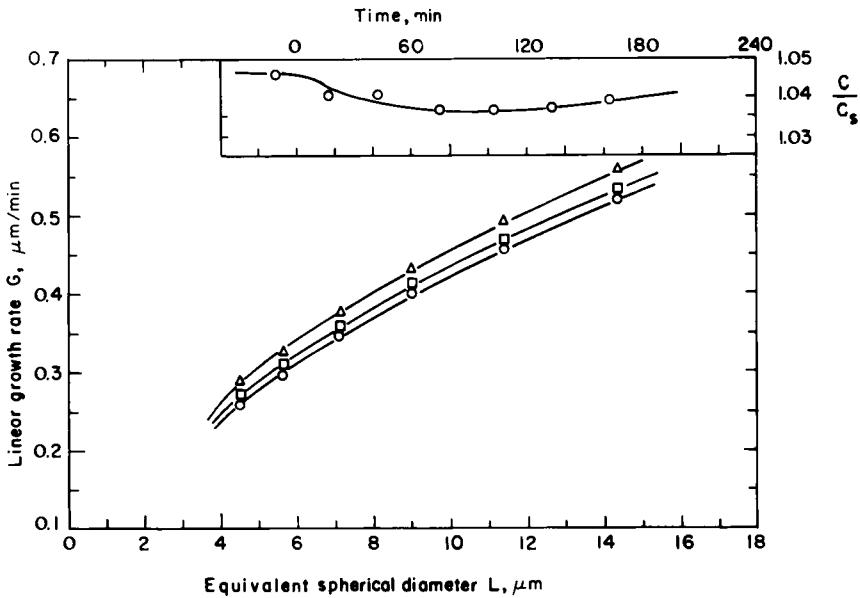


Fig. 9.6-3 Growth rate versus particle size for small K_2SO_4 crystals; $\tau = 180$ (Δ), 120 ($\square$), 60 ($\circ$) min [M. D. Cise, and A. D. Randolph, Paper 39d, 3rd Joint Meeting, AIChE-IMI, Denver, Colorado, 1970].

Extensive studies on the K_2SO_4 and $(NH_4)_2SO_4$ systems have been conducted using this apparatus. Figure 9.6-3 plots crystal growth rate versus size for the K_2SO_4 system under typical process conditions. Levels of supersaturation are shown by the insert. These data are consistent with the size-dependent growth rates observed for K_2SO_4 in other MSMPR studies. However, some of the character of these data might be explained as an artifact caused by an actual birth function of secondary nuclei, $B(L)$, over the measured size range. Such a birth function was assumed to be zero in the analysis of these data. Figure 9.6-4 plots transient fine-crystal populations from which these growth rate data were obtained. Notice the ever-increasing population densities of these fines due to the growth in the totally retained secondary nucleation environment. The ever-increasing secondary environment necessitates use of a multichannel counter to measure the entire distribution in a brief sampling time. Again, the extremely rapid rise in population density at the smaller sizes could have been interpreted as due to a birth function over this size range. Sources of error and extraneous noise in the particle counter were exhaustively examined to eliminate the counting technique as a likely cause of high population counts in the smaller size ranges.

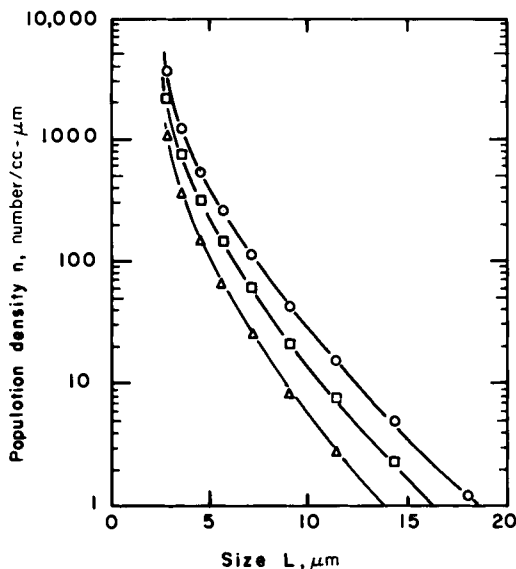


Fig. 9.6-4 Population density versus size for K_2SO_4 crystals at three measurement times—180 (○), 120 (□), and 60 (△) min—after introduction of seed crystals [M. D. Cise and A. D. Randolph, Joint Meeting AIChE and IMIQ, 3rd, Denver, Colorado, September 1970. Paper 39d].

9.7 Summary

We have described here some of the apparatus which have been used to measure crystallization kinetics in mixed suspensions and have listed some of the data which have been taken under these conditions. Representative data from cooling, evaporative, and precipitation crystallizers have been included. Separate growth studies have not been reported because of the extensive availability of these data in the literature. We suggest that the data given here are most useful in predicting size distribution from mixed suspension crystallizers operating with conditions close to those existing in these studies. Data taken in the manner described on other systems should prove useful in the understanding and prediction of CSD in such systems.

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APPLICATION TO OTHER SYSTEMS

We have seen in previous chapters how the population balance can be used to analyze size distributions of crystals obtained from processes where crystal nucleation and growth are occurring simultaneously. The numbers (population) balance is of considerable utility in analysis of other systems composed of countable entities. There are many examples in the process industries where discrete entities are created, destroyed, or changed in some way as a result of processing. Many biochemical processes have characteristics which lend themselves to analysis via the population balance. Even plant, animal, or human populations can be represented in time, place, and state space in the same manner as are crystal-size distributions.

In this chapter, we review some of the literature already available which shows how the numbers balance has been of use in predicting particle-size distributions in grinding processes and in characterizing polymerization processes, microbial processes, age distributions, dispersed-phase liquid systems, agglomeration, and demographic population distributions.

10.1 Comminution Processes

Comminution can represent one of the major costs of mineral recovery. Efficient mineral recovery in a typical low-grade ore grinding–flotation process depends on grinding the ore small enough to liberate mineralization

without producing excessive slimes, which would result in higher power and flotation reagent costs. Size criteria for efficient grinding should be stated in terms of the distribution of mineralization sizes, but as the mineralization-size distribution varies, less desirable criteria of absolute particle-size distribution (PSD) are used in practice. Thus, there is considerable incentive to be able to analyze and predict the PSD performance of grinding circuits for control and optimization of the process.

Most previous studies of the grinding unit operation attempt to relate power consumption and sizing scale factors to the ore hardness, throughput, and size reduction occurring in various types and configurations of grinding equipment. The PSD obtained was tested experimentally; however, the basic equations did not attempt to predict PSD as a function of process parameters, but rather, concentrated on process sizing and energy requirements of equipment which would be adequate for the desired amount of size reduction.

The theory of particulate processes developed in this book is suitable for development of input-output PSD models of a grinding mill, which, given an empirically correct representation of the birth and death functions, can predictively model PSD. Development of suitable birth and death functions is, of course, central to the success of such predictive PSD models. The population balance provides a convenient formalism for insertion of such continuous breakage functions so that interactions with process configurations and/or transients can be easily modeled.

Previous PSD models of grinding mills have been developed from mass balance considerations and are phrased in terms of discrete, rather than continuous, size ranges. Both kinetic and purely probabilistic approaches have been used. The probabilistic breakage and selection matrix approach models the PSD of a fixed-configuration operating mill by writing a set of matrix equations relating the mass fractions in discrete size ranges. The selection matrix **A** represents the mass fraction in each discrete size range that break into a lower size, while the breakage matrix **B** represents the mass fraction from each breakage event that go to a lower size fraction. Elementary mass balance considerations relate the selection and breakage matrices as shown in Fig. 10.1-1 to generate PSD from the mill. There is little predictive value in this probabilistic approach; no process parameters or throughputs are included with the matrices and the elements of **A** and **B** must be obtained *post facto* by fitting PSD data under the specific mill conditions. Some attempts have been made to link the matrix elements with ore type and operating conditions, but these efforts have met with little success.

More recent PSD models for grinding mills have combined discrete kinetic breakage models, stated probabilistically and similar to those in the matrix approach, with mass balances over specific process configurations to predict the resultant PSD in that configuration. These kinetic approaches to modeling

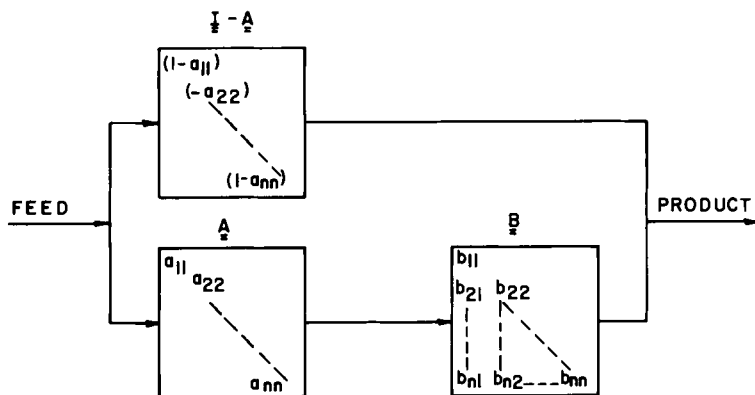


Fig. 10.1-1 Schematic representation of probabilistic matrix approach [Preprint 71-B-78, AIChE Meeting, New York, March, 1971].

have the potential for predictive PSD studies through the interaction of residence-time distribution in the system (process configuration) with the empirical breakage and selection kinetics. The model is calibrated by adjusting either the selection and breakage kinetic constants or the idealized process configuration (e.g., the number of hypothetical staged tanks in series) until the experimental PSD is matched.

The breakage kinetic rate constant can be measured directly from batch grinding data and such studies usually indicate that breakage can be represented by simple first-order kinetics of the form

$$dm_j/dt = Km_j \quad (10.1-1)$$

where m_j is the mass in the j th discrete size range. Measurement and formulation of breakage functions representing the distribution of pieces from a given breakage event are more difficult tasks; such information is usually obtained by calibrating a specific breakage model to experimental PSD data.

There is little difficulty in generalizing the mass-balance-derived kinetic models described above to a continuous-size model linked with process flow configurations of arbitrary complexity. However, the population balance in particle phase space provides just such a generalized formalism and has been used to generate continuous PSD models [1]. Two forms of the population balance are applicable; the micro-distributed and macro-distributed forms describing one-dimensional particle-size distributions in spatially distributed and backmixed systems, respectively. Variations in residence-time distribution between the plugflow and backmixed idealizations can be approximated with classified removal from a backmixed system. Thus, with little loss in

generality, the population balance (slurry basis) for a grinding mill can be written [see Fig. 3.5-1 and Eq. (3.5-22) in Section 3.5] as

$$dn/dt = B(L) - D(L) - (Q_F n_F/V) + \{[P(L) - 1]V\} Q_o(L)n$$

where $P(L)$ is the size-classification function of the oversize separator and $Q_o(L)$ is an equivalent size-dependent removal rate which shapes the residence-time distribution in the system. Continuous empirical breakage functions B and D must of course be phrased for the system. As shown in Section 7.5, the birth function must be consistent with the assumed death function and can be cast in a form to conserve either particle length, as [Eq. (7.5-8a)]

$$B(L) = 2L \int_0^1 [P(\varepsilon, \xi) D(L/\varepsilon) d\varepsilon/\varepsilon^2]$$

or particle mass, as [Eq. (7.5-8b)]

$$B(L) = 6L^3 \int_0^1 [P_m(\varepsilon^3, \xi) D(L/\varepsilon) d\varepsilon/\varepsilon^2]$$

but not both length and mass at the same time.

The unique features of PSD modeling based on the population balance theory of particulate systems are as follows:

- a. The equations are continuous in particle size L , thus requiring more sophisticated solution techniques but yielding more information.
- b. The number of adjustable parameters can be reduced relative to matrix coefficients, by adroit selection of the form of the breakage functions.
- c. The independent effects of process configuration and breakage kinetics are separated and easily identifiable.
- d. Transient PSD can be predicted by merely retaining the dn/dt term and allowing other parameters to assume dynamic values.
- e. The model can be implemented in as elementary or as sophisticated a manner as necessary to fit the problem without rederiving the equations.

EXAMPLE 10.1-1

Using input-output PSD data from an open-circuit industrial ball mill and the population balance for a single backmixed stage, find the coefficients in the simple two-parameter death function of Example 7.5-1. Use a consistent birth function which assumes the broken pieces are randomly distributed along the length axis, i.e., Eq. (7.5-8a) together with the uniform

probability distribution shown in Fig. 7.5-1a. Using the parameters determined from one set of data, predict and compare PSD to that obtained with different feed distribution and feed rate. Equation (3.5-22) can be reduced to the ideal backmixed case by allowing the equivalent size-dependent removal rate $Q_o(L)$ to be constant at the mill throughput Q . Further, the open-circuit, steady-state behavior of the mill is to be simulated and thus the classification recycle function $P(L)$ and the transient population term dn/dt are both set equal to zero. The resulting equations describing the system can be written as

$$[(n_F - n)/\tau] + B - D = 0 \quad (10.1-2)$$

where

$$D = knL^\beta \quad (10.1-3)$$

$$B = 2kL^\beta \int_0^1 [n(L/\varepsilon) d\varepsilon/\varepsilon^{(\beta+1)}] \quad (10.1-4)$$

where $\tau = V/Q$, the retention time of slurry in the mill.

Solving for $n(L)$ from (10.1-2)–(10.1-4) gives the integroalgebraic equation

$$n(L) = \left[n_F(L) + 2k\tau L^\beta \int_0^1 \frac{n(L/\varepsilon) d\varepsilon}{\varepsilon^{(\beta+1)}} \right] / (1 + k\tau L^\beta) \quad (10.1-5)$$

Note that the characteristic grinding factor is the product of the breakage rate constant and the slurry retention time. When this product $k\tau$ approaches zero, no grinding occurs and $n \rightarrow n_F$ in Eq. (10.1-5), as would be expected physically. Note also that Eq. (10.1-5) contains two adjustable parameters, k and β , the breakage rate constant and breakage selectivity factor, respectively. A different hierarchy of model arbitrariness is represented by assuming the form of the birth function (uniform distribution of pieces along L space) and a perfectly backmixed stage. If no consistent fit of the data can be made with the two adjustable parameters k and β , then some of these idealizations in the distribution of birth events and/or in residence-time distributions must be relaxed.

Figure 10.1-2 shows the effect of the grinding rate constant k for the case $\beta = 1$ and for typical ore feed distribution (shown in Fig. 10.1-2 for case $k = 0$) and mill throughput. Increases in k produce a finer grind, as expected, and alter the curvature of the distribution. Figure 10.1-3 plots the effect of the selectivity parameter β for $k = 1$ and for the same feed distribution and mill throughput. Note that smaller β values produce a finer grind. Smaller values of β in effect weight the grinding process toward the smaller sizes, where a higher population exists, thus producing a finer grind.

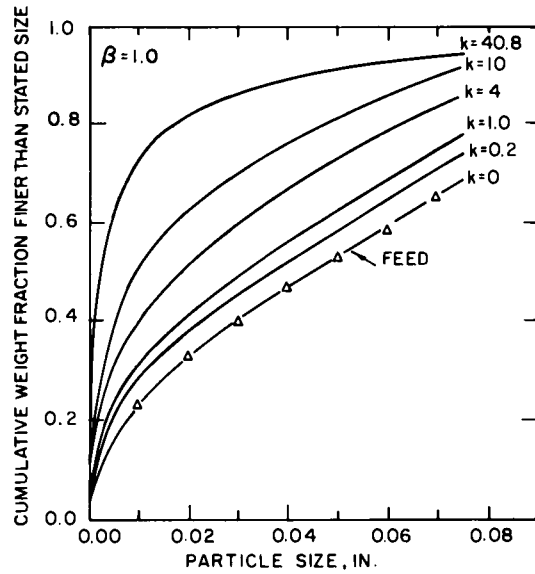


Fig. 10.1-2 Effect of parameter k on model solution [Preprint 71-B-78, AIME Meeting, New York, March, 1971].

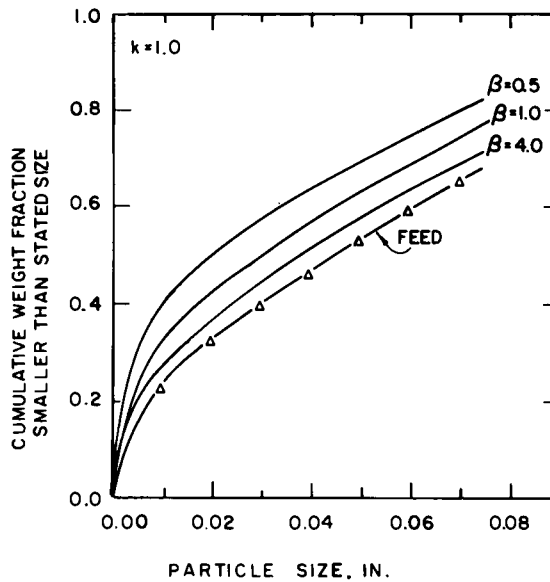


Fig. 10.1-3 Effect of selectivity parameter β on model solution [Preprint 71-B-78, AIME Meeting, New York, March 1971].

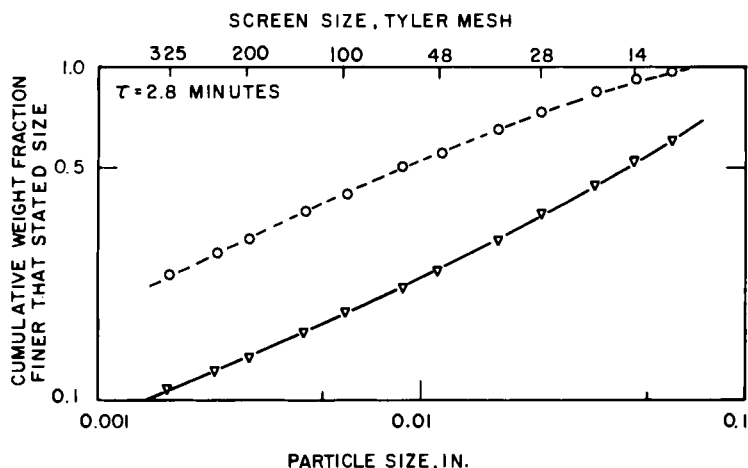


Fig. 10.1-4 Experimental verification of grinding model. Circles: experimental; triangles: feed; Dashed curve: predicted using constants from $\tau = 4.0$ min case [Preprint 71-B-78, AIME Meeting, New York, March, 1971].

Five sets of grinding data¹ from a commercial ball mill operating with slurry residence time of 2.8–4.0 min were analyzed. These residence times correspond to throughputs ranging from 112 to 80 ton/hr of ore. The run at 80 ton/hr, corresponding to $\tau = 4.0$ min, was simulated with the model to fit the output PSD. The optimum choice of parameters based on this 4-min retention run was found to be $k = 800$ and $\beta = 3$. The predictive value of the model was tested by simulating PSD with different feed rates and feed distributions using these same values of k and β . Prediction of PSD for different operating conditions was excellent. Figure 10.1-4 shows the excellent agreement between experimental and predicted PSD for the maximum-throughput case ($P = 112$ ton/hr, $\tau = 2.8$ min) predicted from parameters obtained by analyzing data at the lower throughput.

The model appears to be useful in both a data-fitting and predictive sense. Enormous simplification over previous grinding models was obtained by compressing the breakage empiricism into the two parameters k and β . ♦

10.2 Emulsion Polymerization

The population balance is applicable for the analysis of polymerization processes both at the particulate level and the molecular level. There are four types of polymerization which can be considered: bulk, solution, suspension,

¹ Magnetite copper ore. Data taken at Kennecott Copper Corp., Hurley, New Mexico, Chino Mines Division, released courtesy of the Kennecott Copper Corporation.

and emulsion. Of these, the one most similar to crystallization for analysis purposes is emulsion polymerization considered at the polymer particle level. Polymerization has been treated at the molecular level considering a population balance of molecules of different chain lengths.

A direct application of the general macroscopic population balance was made by Funderburk [2] and Stevens. They modeled the unsteady-state behavior of the size distribution of styrene beads produced by emulsion polymerization. The development which follows was taken from their work.

According to Gardon [3], batch polymerization processes consist of three intervals. During interval I, monomer droplets, soap micelles, and growing polymer particles are present in the aqueous medium. During interval II, soap micelles have either become growing particles or have been adsorbed by growing particles. Interval III begins after all monomer droplets have been consumed. In a continuous system, only interval I is of interest.

We consider a continuous, well-stirred tank or backmixed polymerizer with product streams of the same characterization as the latex in the polymerizer. The latex is defined as an arbitrary polymer particle suspension such that (a) the input and output streams are perfectly mixed; (b) the particle sizes are considered to be distributed continuously over a given size range in an element of latex volume; (c) no splitting or coalescence of particles occurs.

For a system of constant volume and with no particles in the input stream, Eq. (3.5-10) becomes

$$(\partial n / \partial t) + [\partial (n G_v) / \partial v] + (Q/V) n = 0 \quad (10.2-1)$$

Here, the number density is based on the volume of the polymer particle and has units of number per unit volume per unit volume of suspension. As a consequence, the growth rate G_v is a particle volumetric growth rate. Because particles are not destroyed, there is no death function. Birth occurs at "zero" size, and therefore, as in crystallization, the birth rate may be introduced as a boundary condition.

[Alternately, the population density is sometimes based on the particle radius r , and the radial growth rate G_r . Hence,

$$(\partial n / \partial t) + [\partial (n G_r) / \partial r] + (Q/V) n = 0 \quad (10.2-2)$$

The different forms arise because of the various proposed kinetic models for birth and growth.]

The steady-state solution to Eq. (10.2-1) is

$$n = n^0 \exp \left\{ - \int [(1/G_v) (dG_v/dv) + (1/\tau G_v)] dv \right\} \quad (10.2-3)$$

where $\tau = Q/V$ and n^0 is the population density of the "zero"-size beads and is related to birth rate according to the equation

$$B^0 = n^0 G_v \quad (10.2-4)$$

Similarly, for an analysis based on the radius of the polymer particles,

$$n = n^0 \exp \left\{ - \int [(1/G_r) (dG_r/dr) + (1/\tau G_r)] dr \right\} \quad (10.2-5)$$

In order to obtain explicit size distributions, the growth-rate dependence on size must be known. Growth models showing growth dependence on particle size for styrene beads have been developed by Smith and Ewart [4], Medvedev [5], and Stockmayer [6]. These models are given in Table 10.2-1 based both on particle volume and radius. Using these models in Eqs. (10.2-3) and (10.2-5) gives the size distributions shown in Table 10.2-2. These have yet to be confirmed experimentally for a continuous polymerizer.

TABLE 10.2-1
Kinetic Growth Rate Models^a

Model	Volumetric (G_v)	Radial (G_r)
Smith-Ewart	$G_v = 0.5K$ $dG_v/dV = 0$	$G_r = K/8\pi r^2$ $dG_r/dr = -K/4\pi r^3$
Medvedev	$G_v = k_M v^{2/3}$ $dG_v/dv = 2k_M/3v^{1/3}$	$G_r = k_M/(36\pi)^{1/3}$ $dG_r/dr = 0$
Modified Stockmayer	$G_v = KQ$ $dG_v/dv = K(dQ/dv)$	$G_r = KQ/4\pi r^2$ $dG_r/dr = (K/4\pi) [(-20/r^3) + (1/r^2)(dQ/dv)]$
where $dQ/dv = (K'/4v^{1/6}) [bI_1^2(b) + 2I_1(b)I_0(b) - bI_0^2(b)]/I_1^2(b)$		
$K' = 11.41(RN_A/Sk_t)^{0.5}$		

^a J. O. Funderburk, Design models for continuous emulsion polymerization, Ph.D. Thesis, Iowa State Univ., Ames, Iowa, 1969, unpublished.

TABLE 10.2-2*Analytic Solutions for Population Density^a*

Model	Volumetric
Smith-Ewart	$n = n^0 \exp[-(v - v^0)/\tau G_v]$
Medvedev	$n = n^0 \exp\{\ln(v^0/v)^{3/2} - 3[v^{1/2} - (v^0)^{1/2}]/\tau k_p\}$
Modified Stockmayer	$n = n^0 \exp\left[\ln(G_v^0/G_v) - \int_{v^0}^v dv/G_v \tau\right]$
Model	Radial
Smith-Ewart	$n = n^0 \exp\{\ln(r^0/r)^2 - (8\pi/3k\tau)[r^3 - (r^0)^3]\}$
Medvedev	$n = n^0 \exp[(r^0 - r)/G_r \tau]$
Modified Stockmayer	$n = n^0 \exp\left[\ln(G_r^0/G_r) - \int_{r^0}^r dr/G_r \tau\right]$

^a J. O. Funderburk, Design models for continuous emulsion polymerization, Ph.D. Thesis, Iowa State Univ., Ames, Iowa, 1969, unpublished.

In a continuous polymerizer at steady state, the particle nucleation rate must equal the number rate of withdrawal, and hence

$$B^0 = \left(\int_0^\infty n \, dv \right) / \tau \quad (10.2-6)$$

This equals $n^0 G_v$ for the Smith-Ewart model and $n^0 G_r$ for the Medvedev model when a radius-dependent representation is used.

An independent kinetic model for nucleation can be obtained by assuming all radicals produced by the initiator are absorbed through the surface area of the emulsifier. If one assumes also that the surface area is the sum of the surface areas of the polymer particles and micelles, then all radicals not adsorbed by the particles must be adsorbed by the micelles to produce nuclei. The rate of nucleation is then given by the rate of adsorption by the micelles, or

$$B^0 = R \left[1 - (4\pi/A) \int_0^\infty r n \, dr \right] \quad (10.2-7)$$

where R is the rate of radical production per cubic centimeter of aqueous phase and is independent of the amount of initiator present; A is the interfacial area of emulsifier per unit volume. Equation (10.2-6) can now be used to determine the parameters in Eq. (10.2-7).

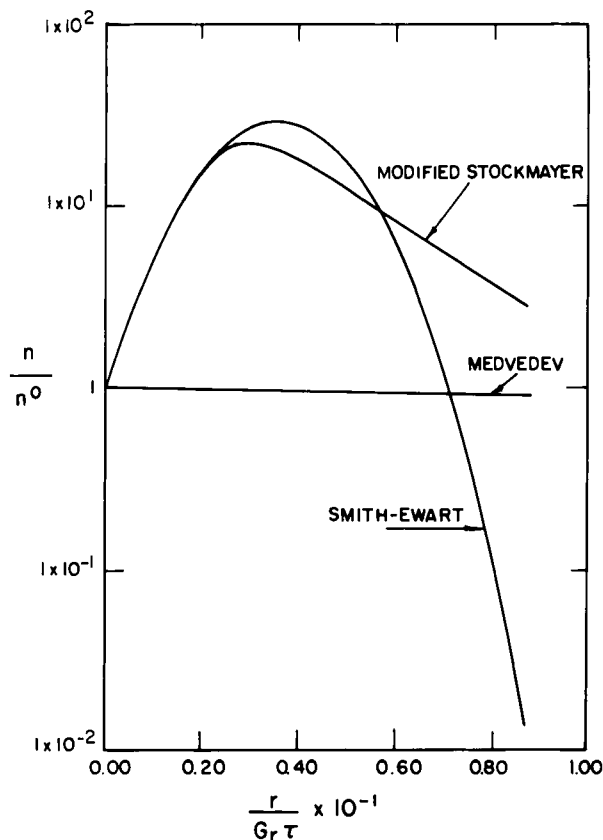


Fig. 10.2-1 Predicted polymer bead size distribution based on bead radius [J. O. Funderburk, Ph.D. Thesis, Iowa State Univ., Ames, Iowa, 1969, unpublished].

Various kinetic models give a variety of predicted size distributions. These are shown in dimensionless form in Figs. 10.2-1 and 10.2-2. The various models for growth predict strikingly different distributions.

The moments of the distributions can be used to determine the mean size of the beads as follows:

$$\bar{v} = \int_0^{\infty} v n \, dv / \int_0^{\infty} n \, dv \quad (10.2-8)$$

A similar expression can be used to determine the mean size based on the radius.

This appears to be a fruitful field for further work, as the subsequent processing properties of the polymer beads are highly dependent on their size distribution.

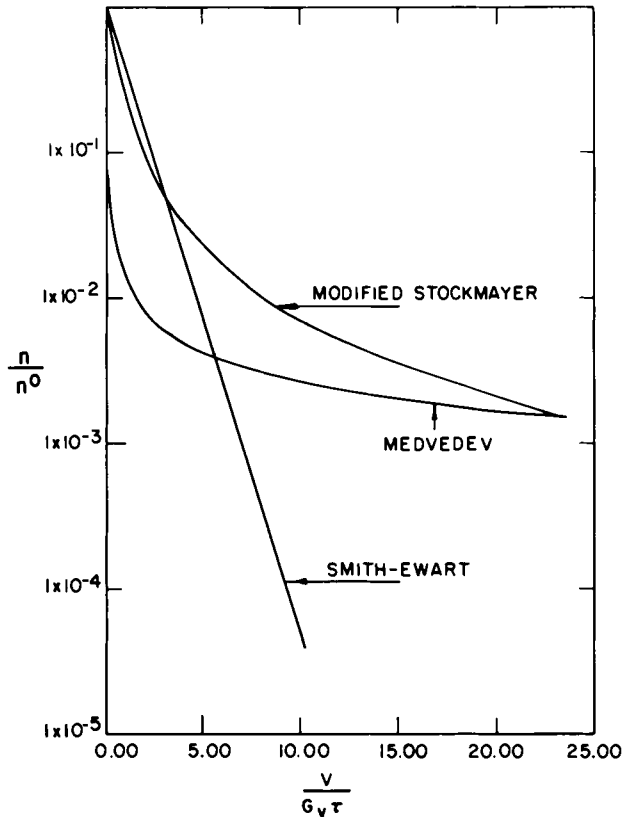


Fig. 10.2-2 Predicted polymer bead size distribution based on bead volume [J. O. Funderburk, Ph.D. Thesis, Iowa State Univ., Ames, Iowa, 1969, unpublished].

10.3 Microbial Populations

The birth, growth, and death rates of microorganisms in biochemical processes can be modeled with the aid of the population balance. The work of Tsuchiya *et al.* [7] forms the basis for the analysis of such systems and will be summarized here. We will show how the treatment relates to the general population balance developed in Chapter 3.

This system is somewhat more complex than a crystallization system in that cell death must be accounted for and birth occurs at a measurable mass. We assume that new entity formation (birth) results from the division of cells into two parts of substantially equal mass.

We consider a well-mixed fermentor in which resides a growing culture of

microorganisms. We chose to characterize the cell by mass rather than by radial dimension. Thus, the population density is defined as

$$n = \lim_{\Delta m \rightarrow 0} (\Delta N / \Delta m) \quad (10.3-1)$$

Let the cell growth rate be represented by G , where

$$G = G(m, C) \quad (10.3-2)$$

and has the dimensions of mass/unit time. Alternately, the age of the cell might be used for characterization, but Koch and Schawchter [8] have shown that mass is a better predictor of division (hence birth) than is age. Using these definitions, Eq. (3.5-10) becomes

$$(\partial n / \partial t) + [\partial (Gn) / \partial m] + D - B = (Q/V) (n_i - n) \quad (10.3-3)$$

where D and B are death and birth functions relating these rates to the cell mass m .

Birth occurs by division of large cells and the rate is formulated as follows: the fraction Γ of cells of mass m that divide in time dt is given by

$$\Gamma = D_f(m, C) dm / n(m)$$

where C is the concentration of the nutrient required for growth; and $P(\xi, m) dm$ is the probability that an original cell of mass ξ undergoing fission will result in a daughter cell of size m . For every fission, two cells result. Thus, the rate at which new daughter cells are obtained, the birth function, is given as

$$B(m) dm = 2 \int_m^\infty P(\xi, m) D_f(\xi) d\xi dm \quad (10.3-4)$$

Death occurs in two ways: as a result of fission and true biological death. The rate of the former is simply

$$D_f dm = \Gamma(m, t) n(m, t)$$

For the latter, we define $T(m, C) dt$ as the fraction of cells of mass m that die in time period dt . The total death-rate function is then

$$D = \Gamma(m, t) n(m, t) + T(m, t) n(m, t) \quad (10.3-5)$$

Substituting into the original number balance gives

$$\frac{\partial n}{\partial t} + \frac{\partial(Gn)}{\partial m} + \left(\Gamma + T + \frac{Q}{V} \right) n = 2 \int_m^\infty n(\xi) \Gamma(\xi) P(m, \xi) d\xi \quad (10.3-6)$$

This equation accounts only for living cells. To completely describe the total population including biologically dead cells, another equation is required. Let n' represent the number density of dead cells. A number balance assuming no introduction of dead cells is

$$\partial n' / \partial t = B' - (Q/V) n' \quad (10.3-7)$$

Dead cells do not grow, nor do they die. The "birth function" B' is the biological death function of Eq. (10.3-6); hence, the population of dead cells is given dynamically as

$$\partial n' / \partial t = \int_0^\infty T(m, t) n(m, t) dm - (Q/V) n' \quad (10.3-8)$$

10.4 Particle Agglomeration

The details of the analysis of particle agglomeration processes, such as those used in the mixed fertilizer industry, are quite different from those we have previously considered. The objective of such processes is to build larger particles by "sticking together" two or more smaller particles. The particles which come together are all of measurable size; therefore, the growth of an agglomerate takes place in finite steps. Except in cases where precipitation takes place on the surface of the agglomerate, continuous growth does not occur and the corresponding term is absent from the model. The size-distribution change is wholly a function of particle birth and death, and particle inflow to and outflow from the system.

Hulburt and Katz [9] considered the case of a plugflow agglomerator where the size distribution must be considered a function of axial position as well as time. Hence, we define the number density as a function of axial position x , mass m , and time t :

$$n = n(x, m, t) \quad (10.4-1)$$

It is assumed here that the distribution does not vary in the radial direction.

In order to model this situation, it is necessary to start with Eq. (3.4-6), the micro-population balance, because the number density is a function of

position as well as state and time. The balance becomes

$$(\partial n / \partial t) + u_x (\partial n / \partial x) = h(x, m, t) \quad (10.4-2)$$

Here, h represents the net rate of formation at size m , i.e.,

$$h(x, m, t) = B - D \quad (10.4-3)$$

Note that no growth term appears. The second term is the flow velocity u_x multiplied by the rate of change of number density with position. It represents the change in size distribution with position along the axis of the agglomerator.

Hulburt and Katz proposed a mechanistic model for birth and death as follows: Particle nucleation under the influence of the chemical environment is ignored. Only particle birth due to collisional agglomeration is considered. At some time t and position x , we let the rate of agglomeration of particles of mass m_1 and m_2 be proportional to the product of the number densities $n(x, m_1, t)$ and $n(x, m_2, t)$. The proportionality factor for collision $a(x, t)$ depends only on the environment and not on the particle size or shape. Thus, particles of mass m will be formed at the rate

$$B(m) = \frac{1}{2} a(x, t) \int_0^\infty n(x, m - \xi, t) n(x, \xi, t) d\xi \quad (10.4-4)$$

where ξ is the mass of one of the colliding particles and $m - \xi$ is the mass of the other. The factor $\frac{1}{2}$ ensures that collisions are not counted twice. Particles of mass m will be lost by agglomeration at the rate

$$D(m) = a(x, t) n(x, m, t) \int_0^\infty n(x, \xi, t) d\xi \quad (10.4-5)$$

Incorporating these two functions into the population balance gives

$$\begin{aligned} (\partial n / \partial t) + u_x (\partial n / \partial x) = & a \left[\frac{1}{2} \int_0^\infty n(x, m - \xi, t) n(x, \xi, t) d\xi \right. \\ & \left. - n(x, m, t) \int_0^\infty n(x, \xi, t) d\xi \right] \end{aligned} \quad (10.4-6)$$

The flow velocity u_x must be obtained from a momentum balance on the system, and the factor $a(x, t)$ reflects the chemical and thermal environment and is related to the external material and energy balances.

The moments of the distribution are defined as

$$m_j = \int_0^\infty p^j n(x, p, t) dp \quad (10.4-7)$$

where p is a dummy of integration. This moment transformation can be used to reduce Eq. (10.4-6) to

$$(\partial m_0 / \partial t) + u_x (\partial m_0 / \partial x) = -\frac{1}{2} a m_0^2 \quad (10.4-8)$$

for $j = 0$.

The solution to Eq. (10.4-8) gives the time and space variance of the total number of agglomerates, i.e., the total number of particles per unit volume as a function of axial dimension x at some point in time.

10.5 Residence-Time Distributions

The concept of residence-time distributions in flow processing vessels as summarized by Danckwerts [10], Wolff and Resnick [11], and others is related to the population distribution we discuss in this volume. We consider first a well-stirred flow reactor with a feed and discharge consisting of a single phase. The “discrete entity” is regarded as an arbitrarily small element of the liquid phase which we shall imagine retains its integrity during its journey through the vessel. Because the vessel is perfectly mixed, we do not concern ourselves with the spatial position of these particles. We characterize the particle only by its state, namely its age, that is, the time it has been in the vessel.

The population density function now becomes a function of time and a function of the age of the element. We distinguish between “age” and time because the age distribution can in general vary in time. This gives

$$n = n(t, \theta)$$

where θ is the age in the environment of the element and n is now thought of as a density fraction of entities in the age range $\theta + d\theta$ such that the number of elements with current residence θ in the environment is given as $N_T n d\theta$, where N_T is the total number of elements in the system.

For the case of a single-stage, perfectly mixed vessel, Eq. (3.5-10) becomes

$$(\partial n / \partial t) + (\partial n / \partial \theta) + (n / \tau) = N Q \delta(\theta) / V \quad (10.5-1)$$

There are no birth or death terms and all input elements enter at age zero; thus, the input term becomes $(N/V)Q\delta(0)$, where N can be thought of as the concentration of elements per unit volume of inflow, Q is the inflow rate V is the volume of the vessel, and $\delta(0)$ is the unit impulse. We note that age is gained in a one-to-one correspondence with the passing of time, so the "growth term" coefficient is unity.

If we specify an initial condition on the distribution, namely $n(0, \theta)$, then Eq. (10.5-1) can be solved to give

$$n(t, a) = \exp(-t/\tau) n(\theta - t, 0) + (N/\tau) \exp(-a/\tau) [U(\theta) - U(\theta - t)] \quad (10.5-2)$$

where $U(\theta)$ is the unit function such that

$$U(\theta) = \begin{cases} 0, & \theta < 0 \\ 1 & \theta > 0 \end{cases} \quad (10.5-3)$$

For a well-mixed vessel at steady state, Eq. (10.5-3) reduces to

$$n = (N/\tau) \exp(-\theta/\tau) \quad (10.5-4)$$

the classic residence-time distribution function for a well-mixed vessel.

The zeroth moment,

$$m_0 = \int_0^\infty n(\theta) d\theta = N[1 - \exp(-\theta/\tau)] \Big|_{\theta=0}^{\theta=\infty} = N_T \quad (10.5-5)$$

gives the total number of elements of all ages in the system. The first moment divided by the zeroth moment gives the average age of all elements, namely the mean residence time τ :

$$\frac{m_1}{m_0} = \frac{\int_0^\infty (N/\tau) \theta \exp(-\theta/\tau) d\theta}{\int_0^\infty (N/\tau) \exp(-\theta/\tau) d\theta} = \frac{N\tau}{N} = \tau \quad (10.5-6)$$

For distributed flows, one must start with Eq. (3.4-6), which accounts for spatial variation of the distribution.

10.6 Dispersed-Phase Mixing

In fluid-fluid contacting operations, one fluid is dispersed in a continuous

phase in the form of droplets or bubbles. It is of interest to characterize the properties of these droplets in order to relate these properties to the rate of mass transfer or chemical reaction which may occur in a process. The droplets may be of different size and of different solute concentration. The distribution of these drops in the property state space in all of the drop properties can be represented by using the basic macroscopic population balance, Eq. (3.5-10),

$$\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{v}_i n + n \frac{d(\log V)}{dt} = B - D - \sum \frac{Q_k n_k}{V}$$

Curl [12] discussed a continuous-flow, dispersed-phase reactor of constant volume where a reaction of arbitrary order takes place by a reactant which is in the dispersed phase. The reactor was assumed to be macroscopically well mixed, that is, the distribution of the dispersed phase was "uniform" throughout the vessel. The droplet distribution was characterized by the reactant concentration in each droplet and the droplet size was assumed to be uniform throughout the reactor. Taking $n = n(C, t)$ and regarding n as the number frequency rather than the population density (i.e., at steady state, $\int_0^\infty n dC = 1$), Eq. (3.5-10) becomes

$$\frac{\partial n}{\partial t} - k \frac{\partial (C^s n)}{\partial C} = B - D + \frac{n_0}{\tau} - \frac{n}{\tau} \quad (10.6-1)$$

Here, the second term represents the rate of change of concentration in the droplets of the distribution due to chemical reaction of order s . The terms n_0/τ and n/τ represent the inflow and outflow of droplets, respectively. The quantity k is the reaction rate constant and $\tau = VQ_1/QQ_2$, where Q_1 is the fraction of dispersed phase in the inflow and Q_2 is the fraction in the outflow. Presumably, these two quantities are nearly equal. Because the reactor volume remains constant, the third term of Eq. (3.5-10) does not appear.

Curl considered a dispersion model based on the assumption that only binary collisions occurred and the resulting coalesced droplets immediately redispersed into two droplets of equal size. Letting C_1 and C_2 represent the concentrations of two colliding droplets, respectively, the two droplets resulting from the redispersion will have a reactant concentration $(C_1 + C_2)/2$. This collision and dispersion model results in expressions for B and D as follows:

$$D = (2u/U)n \quad (10.6-2)$$

$$B = (4u/U) \int_0^C n(C - \alpha) n(C + \alpha) d\alpha \quad (10.6-3)$$

The quantity u is the collision rate and U is the total number of droplets in the dispersion; α is a dummy variable.

Substituting into Eq. (10.6-1) gives for the population balance

$$\frac{\partial n}{\partial t} - k \frac{\partial(C^s n)}{\partial C} + \frac{n}{\tau} = \frac{n_0}{\tau} + \frac{2u}{U} \left[2 \int_0^C n(C - \alpha) n(C + \alpha) d\alpha - n \right] \quad (10.6-4)$$

The above equation has no known analytic solution. However, it can be solved numerically for zero-, first-, second-, and perhaps higher-order reactions for assumed values of $2u/U$.

Again the moments of the distribution have significance. For example, the first moment is the average droplet concentration in the suspension:

$$m_1 = \int_0^\infty Cn dC \quad (10.6-5)$$

EXAMPLE 10.6-1

Assume a continuous, backmixed, dispersed system in which reactant A of concentration C in the dispersed phase undergoes a first-order reaction. At steady state and when no collisions occur, u is zero and Eq. (10.6-4) becomes

$$k[d(Cn)/dC] - (n/\tau) = -n_0/\tau \quad (10.6-6)$$

Let $n_0 = -\delta(C - C_0)$,

$$k[d(Cn)/dC] - (n/\tau) = (1/\tau)\delta(C - C_0) \quad (10.6-7)$$

Integrating using the integrating factor $\exp[(k\tau - 1)/k\tau]$ gives

$$n = (1/k\tau C) [C/C_0]^{1/k\tau} \quad (10.6-8)$$

The average concentration $\bar{C}$ is

$$m_1 = \bar{C} = \int_0^C (1/k\tau) (C/C_0)^{1/k\tau} dC \quad (10.6-9)$$

$$\bar{C} = C_0/(1 + k\tau) \quad (10.6-10)$$

We note this is the same result as is obtained from a perfectly mixed system. ♦

EXAMPLE 10.6-2

Repeat Example 10.6-1 assuming a second-order reaction. Here, Eq. (10.6-4) becomes

$$k[d(C^2n)/dC] - (n/\tau) = (1/\tau)\delta(C - C_0) \quad (10.6-11)$$

Equation (10.6-11) can be solved using the integrating factor $C^2 \exp(1/k\tau C)$ to get

$$n = \frac{1}{C^2 k \tau} \exp \left[\frac{1}{k \tau} \left(\frac{1}{C_0} - \frac{1}{C} \right) \right] \quad \blacklozenge \quad (10.6-12)$$

Clearly, it is possible to use other collision and coalescence models as well as other state properties for studying dispersed systems. The difficulty arises in obtaining realistic parameters for representing the collision frequency and dispersion frequency.

10.7 Demographic Analysis

The dynamics of human population change have always been a topic of interest and wonder. The current population pressures in our cities, in many countries, and in the world in general have caused a good deal more interest in the growth and decline of human populations. Not since the gloomy predictions of Malthus has the concern for this problem been as great.

The model used consistently throughout this volume can serve as an analytical framework for demographers in their study of the response of populations to various stimuli.² Of course, as with many population-balance-based studies, the critical factor in the validity and usefulness of such models is the proper formulation and verification of empirical population kinetics.

As an example, let us consider a geographic identity (city or country) whose population may be considered a continuum. That is, if we characterize a person by his age θ , we consider the age distribution of any large segment of the population as a continuous function. Consider the density function $n(t, \theta) d\theta$ to be the population having an age in the interval θ to $\theta + d\theta$ at time t . Further, define $N_i(t, \theta)$ as the number rate of people of age θ entering the system by immigration and $N_e(t, \theta)$ the number rate of people of age θ

² The authors make no claims to expertise as demographers, yet the following discussion and examples, totally hypothetical, illustrate nicely the full formalism of this multivariate distribution theory. These examples are useful from a pedagogical standpoint when this material is taught as a special topic graduate course.

leaving by emigration. Neglecting spatial variations of population within the geographic unit under consideration, Eq. (3.5-10) becomes

$$\frac{\partial n}{\partial t} + v_\theta \frac{\partial n}{\partial \theta} + v_p \frac{\partial n}{\partial p} + D(n, \theta, p) - \delta(\theta - 0) B^0 = N_i(t, \theta, p) - N_o(t, \theta, p) \quad (10.7-1)$$

where B^0 are the births at age zero resulting from the current age distribution of the population and where the convective velocity along the age axis v_θ is identically equal to unity, i.e., $d\theta/dt = 1$. The variable p represents any second orthogonal phase space coordinate. Birth is related to the age distribution of the population and is heavily weighted toward the distribution of ages between, say, 16 and 45. The death function is, of course, related to the whole distribution but is heavily dependent on the age distribution at the older end of the distribution. In either case, functions for these two terms could be obtained accurately from insurance company birth and mortality tables. If a more detailed analysis of the population dynamics is desired, it is clear that two population-age distributions could be computed, one for each sex, forming a coupled set (no pun intended) of equations describing the entire system.

Immigration represents an outside arbitrary disturbance to the system, although the rate N_i might be expected to couple weakly with the current state of the population n . Given a specified immigration function $N_i(t, \theta)$, the dynamic effects on population distribution can easily be determined. Certainly, emigration would be age-dependent. Thus, output from the population unit under consideration might be represented by an age-dependent mean retention probability as $N_o = n(t, \theta)/\tau(\theta)$. Such a formulation is analogous to the crystallization problem of classified withdrawal. By arbitrarily specifying the mean retention probability $\tau(\theta)$, effects of various types of emigration can be determined.

We note that the moments over the age distribution have significance as in the case of other distributions. Thus, total population $N_T(t)$ is given as

$$N_T(t) = \int_0^\infty n d\theta = m_0 \quad (10.7-2)$$

and

$$\bar{\theta} = \int_0^\infty \theta n d\theta / \int_0^\infty n d\theta = m_1/m_0 \quad (10.7-3)$$

where $\bar{\theta}$ is the average age of the population.

The above analysis could be applied to countries, continents, or any geographic, economic, or ethnic group. By returning to the distributed forms of

the population balance given in Chapter 3, one can develop a geographic representation as well. This general representation permits modeling of population–geographic as well as population–age distributions if the appropriate spatial and age dependence of the birth and death rates is known.

Other population phase plane coordinates besides age can be defined, e.g., a coordinate p describing the material wealth of a population segment. The term $n(t, p) dp$ would then represent the number of people in a geographic unit at a given time having wealth in the range p to $p + dp$. Population dynamics in this case could reasonably be influenced by many factors, e.g., continuous net earnings [given by wealth-dependent “growth” rate $v_p = v_p(p)$], transfer between population groups [given by “birth” and “death” terms $B(p)$ and $D(p)$], and wealth-dependent input and output rates [given by input–output terms $N_i = N_i(t, p)$ and $N_o = n(t, p)/\tau(p)$]. Realistically, wealth in population kinetics depends heavily on population age; the dynamic multivariate age and wealth density distribution function $n(t, \theta, p)$ can be described by these techniques given correct information on population kinetics. All total and average properties of interest can be readily calculated from the population density function.

Such dynamic population models would demand the full formalism of the distribution theory presented in this book.

EXAMPLE 10.7-1

Use the macro-population balance to set up equations describing the steady-state population–age distribution and total population of a closed society. Calculate the fraction of original births that are still living at age 70. Assume that population dynamics for this society can be represented statistically by the following equations:

$$\begin{aligned} B^0 &= \int_0^\infty B^0(\theta) d\theta = k \int_0^\infty [n(\theta)/n^0] \rho(\theta) d\theta \\ &= k \int_0^\infty f(\theta) \rho(\theta) d\theta \quad \text{births/year} \end{aligned} \quad (10.7-4)$$

where $B^0(\theta) d\theta$ are the number of births from the adult population of age θ to $\theta + d\theta$, $n(\theta) d\theta$ is the population in age group θ to $\theta + d\theta$, $f(\theta)$ is the fraction of original population left alive in age group θ , $\rho(\theta)$ is a weighting function of age group θ , and k is an overall fertility “inclination” factor which involves the amount of resources available for population growth.

Assume that the weighting factor can be expressed as a log-normal distribution around a median female fecund age of 25 years. Thus,

$$\frac{B^0(\theta)}{kf(\theta)} = \rho(\theta) = \frac{1}{(2\pi)^{1/2} \log \sigma'} \exp \left[-\frac{\log^2(\theta/25)}{2 \log^2 \sigma'} \right] \quad (10.7-5)$$

Approximately $\frac{1}{2}\%$ of each age group dies each year until age 40, when the death frequency increases markedly. These death statistics may be represented by a death function given as proportional to the population density times a polynomial weighting factor. Thus,

$$D(\theta) = 0.005 [1 + 2(\theta/40)^4] n(\theta) \quad \text{deaths/year} \quad (10.7-6)$$

in age group θ . Immigration and emigration from the society can be neglected. The macro population balance, Eq. (10.7-1) simplifies in this case to

$$v_\theta dn/d\theta = -D(\theta) \quad (10.7-7)$$

where $v_\theta = d\theta/dt = 1$. The boundary condition for this equation is

$$n^0 = n(0) = \frac{B^0}{v_\theta} = \frac{k}{(2\pi)^{1/2} \log \sigma'} \int_0^\infty f(p) \exp \left[\frac{-\log^2(p/25)}{2 \log^2 \sigma'} \right] dp \quad (10.7-8)$$

where p is a dummy of integration. Solving (10.7-7) for population density gives

$$dn/n = -0.005 [1 + 2(\theta/40)^4] d\theta \quad (10.7-9)$$

Integrating from $n = n^0$ and $\theta = 0$ gives

$$f(\theta) = n/n^0 = \exp \{ -0.005 [\theta + 2\theta^5/(5)(40)^4] \} \quad (10.7-10)$$

Equations (10.7-8) and (10.7-10) are then solved for the population density, $n(\theta)$. Thus

$$\begin{aligned} n(\theta) &= \frac{k}{(2\pi)^{1/2} \log \sigma'} \int_0^\infty \exp \left\{ -0.005 \left[\frac{p + 2p^5}{(5)(40)^4} \right] - \frac{\log^2(p/25)}{2 \log^2 \sigma'} \right\} dp \\ &\quad \times \exp \left\{ -0.005 \left[\frac{\theta + 2\theta^5}{(5)(40)^4} \right] \right\} \end{aligned} \quad (10.7-11)$$

The total population in the society is given as

$$N_T = \int_0^{\infty} n(\theta) d\theta = n^0 \int_0^{\infty} \exp \left\{ -0.005 \left[\frac{\theta + 2\theta^5}{(5)(40)^4} \right] \right\} d\theta \quad (10.7-12)$$

The fraction of original births still alive at age 70 is

$$\begin{aligned} f(70) &= \exp \{ -0.005 [70 + (2)(70)^5 / (5)(40)^4] \} \\ &= 0.19 \end{aligned} \quad (10.7-13)$$

Thus, 19% of the population is predicted to live to at least 70 years of age. ♦

The above example, although perhaps trivial, illustrates the use of this formalism to study population problems. It should be noted that the function $1000D(\theta)/n(\theta)$ represents the deaths per thousand in any population group of age θ and can be determined directly from actuarial statistics. A polynomial expression, as illustrated above, should prove a fruitful way to correlate these data. The function $1000B^0(\theta)/f(\theta)$ B^0 represents the births per thousand from each population group of age θ . The birth weighting function $\rho(\theta)$ could be assembled directly from actuarial statistics, in this example, by plotting $B^0(\theta)/n(\theta)$ versus θ on log-normal probability paper. Both $B^0(\theta)$ and $D(\theta)$ can be expressed as functions of time by extrapolating actuarial statistics, thus enabling prediction of dynamic population distributions.

In the previous example, the level of population was established with the parameter k . The death function and birth weighting terms merely shaped the form of the age distribution and apportioned the total births, respectively. A difficult problem in demographic analysis is in establishing and predicting the total birth rate (established in this case by the parameter k) as a function of both population resources available and current levels of population.

EXAMPLE 10.7-2

The closed society of Example 10.7-1 is suddenly threatened from without, causing the birth factor k to increase by 10% and the log-normal birth weighting function to widen from a σ' of 1.2 to 1.25. Write the equations describing the dynamic population–age distribution and show their interrelationship in an information flow diagram. Write an equation showing the increase as a function of time in the 5–18-year olds resulting from this change.

The steady-state starting population–age distribution $n_0(\theta)$ is obtained by solution of the steady-state equations in the previous example with $\sigma' = 1.2$ and the original population constant k_0 .

Dynamic population distribution is then described by the following set of equations:

$$\frac{\partial n}{\partial t} + \frac{\partial n}{\partial \theta} = -0.005 \left[1 + 2 \left(\frac{\theta}{40} \right)^4 \right] \quad (10.7-14)$$

$$n(0, \theta) = n_0(\theta) \quad (10.7-15)$$

$$n(t, 0) = \frac{(k_0)(1.1)}{(2\pi)^{1/2}(1.25)} \int_0^\infty f(p) \exp \left[\frac{-\log^2(p/25)}{(2)(1.25)^2} \right] dp \quad (10.7-16)$$

The percentage increase in school-age children in the 5–18-year age group is then given as

$$\text{percent increase} = 100 \int_5^{18} [(n/n_0) - 1] d\theta \quad (10.7-17)$$

Of course, no increase in school-age population would appear in Eq. (10.7-17) until five years after the initial birth rate upset.

An information flow diagram for this population problem is shown in Fig. 10.7-1. ♦

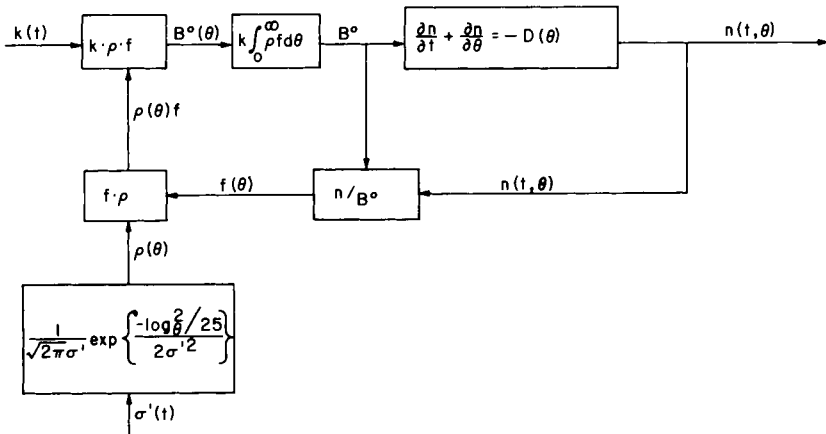


Fig. 10.7-1 Information flow diagram showing adjustments in population–age distribution resulting from changes in population parameters.

10.8 Summary

We have given here brief examples of several population distributions where the analyses used in crystallization could be of use. The treatments have necessarily been brief, and for those taken from other authors, we refer the reader to the original work. The examples chosen are not exhaustive and many others are surely subject to this analysis. We hasten to add that we claim no particular expertise in the fields of polymerization, microbiology, or demography. The birth and death models given in this chapter are not claimed to be representative of any great amount of accumulated data and should therefore be regarded as examples to illustrate a possible application of the population balance.

The analyses and developments in Chapters 2 and 3 are directly applicable to all of these examples. This general population balance should now be studied in the context of the example of interest. The complete analyses of crystallization in Chapters 4, 5, and 7–9 should provide many analogies to the examples listed in these chapters as well as other distribution examples. With these techniques as a starting point, much can be done to improve understanding of the dynamics of population distributions.

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DIMENSIONLESS WEIGHT-FRACTION FUNCTION

A characteristic CSD function which appears in many of the cumulative weight-size distribution equations is the gamma-type function

$$w(x) = \frac{1}{6} \int_0^x \exp(-p) p^3 dp$$

This function naturally arises when the population density is of at least piece-wise exponential form. Thus, consider the population density in a size range L in (a, b) to be given exponentially as

$$n = c_1 \exp(-c_2 L)$$

where a, b, c_1 , and c_2 are constants. The weight fraction occurring in this size range is then given as

$$W(a, b) = \rho k_v \int_a^b n L^3 dL / M_T$$

or

$$W(a, b) = K \int_a^b \exp(-c_2 L) L^3 dL$$

Making the dimensionless substitution $p = c_2 L$ gives

$$W(a, b) = K' \int_{a'}^{b'} \exp(-p) p^3 dp$$

where a' and b' are the dimensionless sizes

$$a' = c_2 a, \quad b' = c_2 b$$

Finally, in terms of the dimensionless weight distribution function,

$$W(a, b) = 6K' [w(b') - w(a')]$$

Thus, the dimensionless $w(x)$ function appears in any calculations of weight-size distribution when the population density is given in terms of exponentials.

The dimensionless $w(x)$ function is given in Table A.1 over the interval x in (0, 10) in increments of 0.1. The function can be easily integrated and can alternately be carried in analytic form as a computational subroutine in CSD algorithms. Thus,

$$w(x) \equiv \frac{1}{6} \int_0^x \exp(-p) p^3 dp = 1 - \exp(-x) (1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3)$$

TABLE A.1

Dimensionless Weight-Fraction Function $w(x) = \frac{1}{6} \int_0^x \exp(-p) p^3 dp$

$w(x)$	x	$w(x)$	x	$w(x)$	x	$w(x)$	x
0.000	0.01	0.002	0.51	0.020	1.01	0.067	1.51
0.000	0.02	0.002	0.52	0.020	1.02	0.068	1.52
0.000	0.03	0.002	0.53	0.021	1.03	0.070	1.53
0.000	0.04	0.002	0.54	0.022	1.04	0.071	1.54
0.000	0.05	0.003	0.55	0.022	1.05	0.072	1.55
0.000	0.06	0.003	0.56	0.023	1.06	0.073	1.56
0.000	0.07	0.003	0.57	0.024	1.07	0.075	1.57
0.000	0.08	0.003	0.58	0.024	1.08	0.076	1.58
0.000	0.09	0.003	0.59	0.025	1.09	0.077	1.59
0.000	0.10	0.003	0.60	0.026	1.10	0.079	1.60
0.000	0.11	0.004	0.61	0.027	1.11	0.080	1.61
0.000	0.12	0.004	0.62	0.027	1.12	0.082	1.62
0.000	0.13	0.004	0.63	0.028	1.13	0.083	1.63
0.000	0.14	0.004	0.64	0.029	1.14	0.084	1.64
0.000	0.15	0.005	0.65	0.030	1.15	0.086	1.65
0.000	0.16	0.005	0.66	0.030	1.16	0.087	1.66
0.000	0.17	0.005	0.67	0.031	1.17	0.089	1.67
0.000	0.18	0.005	0.68	0.032	1.18	0.090	1.68
0.000	0.19	0.006	0.69	0.033	1.19	0.092	1.69

TABLE A.1 (CONTINUED)

$w(x)$	x	$w(x)$	x	$w(x)$	x	$w(x)$	x
0.000	0.20	0.006	0.70	0.034	1.20	0.093	1.70
0.000	0.21	0.006	0.71	0.035	1.21	0.095	1.71
0.000	0.22	0.006	0.72	0.036	1.22	0.096	1.72
0.000	0.23	0.007	0.73	0.036	1.23	0.098	1.73
0.000	0.24	0.007	0.74	0.037	1.24	0.099	1.74
0.000	0.25	0.007	0.75	0.038	1.25	0.101	1.75
0.000	0.26	0.008	0.76	0.039	1.26	0.102	1.76
0.000	0.27	0.008	0.77	0.040	1.27	0.104	1.77
0.000	0.28	0.008	0.78	0.041	1.28	0.106	1.78
0.000	0.29	0.009	0.79	0.042	1.29	0.107	1.79
0.000	0.30	0.009	0.80	0.043	1.30	0.109	1.80
0.000	0.31	0.010	0.81	0.044	1.31	0.110	1.81
0.000	0.32	0.010	0.82	0.045	1.32	0.112	1.82
0.000	0.33	0.010	0.83	0.046	1.33	0.114	1.83
0.000	0.34	0.011	0.84	0.047	1.34	0.115	1.84
0.000	0.35	0.011	0.85	0.048	1.35	0.117	1.85
0.001	0.36	0.012	0.86	0.049	1.36	0.119	1.86
0.001	0.37	0.012	0.87	0.050	1.37	0.120	1.87
0.001	0.38	0.013	0.88	0.052	1.38	0.122	1.88
0.001	0.39	0.013	0.89	0.053	1.39	0.124	1.89
0.001	0.40	0.014	0.90	0.054	1.40	0.125	1.90
0.001	0.41	0.014	0.91	0.055	1.41	0.127	1.91
0.001	0.42	0.015	0.92	0.056	1.42	0.129	1.92
0.001	0.43	0.015	0.93	0.057	1.43	0.131	1.93
0.001	0.44	0.016	0.94	0.058	1.44	0.132	1.94
0.001	0.45	0.016	0.95	0.060	1.45	0.134	1.95
0.001	0.46	0.017	0.96	0.061	1.46	0.136	1.96
0.001	0.47	0.017	0.97	0.062	1.47	0.138	1.97
0.002	0.48	0.018	0.98	0.063	1.48	0.139	1.98
0.002	0.49	0.018	0.99	0.064	1.49	0.141	1.99
0.002	0.50	0.019	1.00	0.066	1.50	0.143	2.00
0.145	2.01	0.245	2.51	0.355	3.01	0.466	3.51
0.147	2.02	0.247	2.52	0.357	3.02	0.468	3.52
0.148	2.03	0.249	2.53	0.360	3.03	0.470	3.53
0.150	2.04	0.251	2.54	0.362	3.04	0.472	3.54
0.152	2.05	0.253	2.55	0.364	3.05	0.474	3.55
0.154	2.06	0.255	2.56	0.366	3.06	0.476	3.56
0.156	2.07	0.258	2.57	0.369	3.07	0.478	3.57
0.158	2.08	0.260	2.58	0.371	3.08	0.481	3.58
0.160	2.09	0.262	2.59	0.373	3.09	0.483	3.59
0.161	2.10	0.264	2.60	0.375	3.10	0.485	3.60
0.163	2.11	0.266	2.61	0.377	3.11	0.487	3.61
0.165	2.12	0.268	2.62	0.380	3.12	0.489	3.62
0.167	2.13	0.271	2.63	0.382	3.13	0.491	3.63
0.169	2.14	0.273	2.64	0.384	3.14	0.493	3.64
0.171	2.15	0.275	2.65	0.386	3.15	0.495	3.65
0.173	2.16	0.277	2.66	0.389	3.16	0.498	3.66
0.175	2.17	0.279	2.67	0.391	3.17	0.500	3.67
0.177	2.18	0.282	2.68	0.393	3.18	0.502	3.68
0.179	2.19	0.284	2.69	0.395	3.19	0.504	3.69

TABLE A.1 (CONTINUED)

$w(x)$	x	$w(x)$	x	$w(x)$	x	$w(x)$	x
0.181	2.20	0.286	2.70	0.398	3.20	0.506	3.70
0.183	2.21	0.288	2.71	0.400	3.21	0.508	3.71
0.185	2.22	0.290	2.72	0.402	3.22	0.510	3.72
0.187	2.23	0.293	2.73	0.404	3.23	0.512	3.73
0.189	2.24	0.295	2.74	0.406	3.24	0.514	3.74
0.191	2.25	0.297	2.75	0.409	3.25	0.516	3.75
0.193	2.26	0.299	2.76	0.411	3.26	0.518	3.76
0.195	2.27	0.301	2.77	0.413	3.27	0.520	3.77
0.197	2.28	0.304	2.78	0.415	3.28	0.522	3.78
0.199	2.29	0.306	2.79	0.418	3.29	0.525	3.79
0.201	2.30	0.308	2.80	0.420	3.30	0.527	3.80
0.203	2.31	0.310	2.81	0.422	3.31	0.529	3.81
0.205	2.32	0.313	2.82	0.424	3.32	0.531	3.82
0.207	2.33	0.315	2.83	0.426	3.33	0.533	3.83
0.209	2.34	0.317	2.84	0.429	3.34	0.535	3.84
0.211	2.35	0.319	2.85	0.431	3.35	0.537	3.85
0.213	2.36	0.321	2.86	0.433	3.36	0.539	3.86
0.215	2.37	0.324	2.87	0.435	3.37	0.541	3.87
0.217	2.38	0.326	2.88	0.437	3.38	0.543	3.88
0.219	2.39	0.328	2.89	0.440	3.39	0.545	3.89
0.221	2.40	0.330	2.90	0.442	3.40	0.547	3.90
0.223	2.41	0.333	2.91	0.444	3.41	0.549	3.91
0.226	2.42	0.335	2.92	0.446	3.42	0.551	3.92
0.228	2.43	0.337	2.93	0.448	3.43	0.553	3.93
0.230	2.44	0.339	2.94	0.450	3.44	0.555	3.94
0.232	2.45	0.342	2.95	0.453	3.45	0.557	3.95
0.234	2.46	0.344	2.96	0.455	3.46	0.559	3.96
0.236	2.47	0.346	2.97	0.457	3.47	0.561	3.97
0.238	2.48	0.348	2.98	0.459	3.48	0.563	3.98
0.240	2.49	0.351	2.99	0.461	3.49	0.565	3.99
0.242	2.50	0.353	3.00	0.463	3.50	0.567	4.00
0.569	4.01	0.659	4.51	0.736	5.01	0.799	5.51
0.570	4.02	0.661	4.52	0.738	5.02	0.801	5.52
0.572	4.03	0.663	4.53	0.739	5.03	0.802	5.53
0.574	4.04	0.664	4.54	0.741	5.04	0.803	5.54
0.576	4.05	0.666	4.55	0.742	5.05	0.804	5.55
0.578	4.06	0.668	4.56	0.743	5.06	0.805	5.56
0.580	4.07	0.669	4.57	0.745	5.07	0.806	5.57
0.582	4.08	0.671	4.58	0.746	5.08	0.807	5.58
0.584	4.09	0.673	4.59	0.747	5.09	0.808	5.59
0.586	4.10	0.674	4.60	0.749	5.10	0.809	5.60
0.588	4.11	0.676	4.61	0.750	5.11	0.811	5.61
0.590	4.12	0.678	4.62	0.751	5.12	0.812	5.62
0.592	4.13	0.679	4.63	0.753	5.13	0.813	5.63
0.593	4.14	0.681	4.64	0.754	5.14	0.814	5.64
0.595	4.15	0.682	4.65	0.755	5.15	0.815	5.65
0.597	4.16	0.684	4.66	0.758	5.16	0.816	5.66
0.599	4.17	0.686	4.67	0.758	5.17	0.817	5.67
0.601	4.18	0.687	4.68	0.759	5.18	0.818	5.68
0.603	4.19	0.689	4.69	0.761	5.19	0.819	5.69

TABLE A.1 (CONTINUED)

$w(x)$	x	$w(x)$	x	$w(x)$	x	$w(x)$	x
0.605	4.20	0.690	4.70	0.762	5.20	0.820	5.70
0.607	4.21	0.692	4.71	0.763	5.21	0.821	5.71
0.608	4.22	0.694	4.72	0.765	5.22	0.822	5.72
0.610	4.23	0.695	4.73	0.766	5.23	0.823	5.73
0.612	4.24	0.697	4.74	0.767	5.24	0.824	5.74
0.614	4.25	0.698	4.75	0.768	5.25	0.825	5.75
0.616	4.26	0.700	4.76	0.770	5.26	0.826	5.76
0.617	4.27	0.701	4.77	0.771	5.27	0.827	5.77
0.619	4.28	0.703	4.78	0.772	5.28	0.828	5.78
0.621	4.29	0.704	4.79	0.773	5.29	0.829	5.79
0.623	4.30	0.706	4.80	0.775	5.30	0.830	5.80
0.625	4.31	0.707	4.81	0.776	5.31	0.831	5.81
0.626	4.32	0.709	4.82	0.777	5.32	0.832	5.82
0.628	4.33	0.710	4.83	0.778	5.33	0.833	5.83
0.630	4.34	0.712	4.84	0.780	5.34	0.834	5.84
0.632	4.35	0.713	4.85	0.781	5.35	0.835	5.85
0.634	4.36	0.715	4.86	0.782	5.36	0.836	5.86
0.635	4.37	0.716	4.87	0.783	5.37	0.837	5.87
0.637	4.38	0.718	4.88	0.784	5.38	0.838	5.88
0.639	4.39	0.719	4.89	0.786	5.39	0.839	5.89
0.641	4.40	0.721	4.90	0.787	5.40	0.840	5.90
0.642	4.41	0.722	4.91	0.788	5.41	0.841	5.91
0.644	4.42	0.724	4.92	0.789	5.42	0.842	5.92
0.646	4.43	0.725	4.93	0.790	5.43	0.842	5.93
0.648	4.44	0.727	4.94	0.791	5.44	0.843	5.94
0.649	4.45	0.728	4.95	0.793	5.45	0.844	5.95
0.651	4.46	0.729	4.96	0.794	5.46	0.845	5.96
0.653	4.47	0.731	4.97	0.795	5.47	0.846	5.97
0.654	4.48	0.732	4.98	0.796	5.48	0.847	5.98
0.656	4.49	0.734	4.99	0.797	5.49	0.848	5.99
0.658	4.50	0.735	5.00	0.798	5.50	0.849	6.00
0.850	6.01	0.889	6.51	0.919	7.01	0.941	7.51
0.851	6.02	0.890	6.52	0.919	7.02	0.942	7.52
0.852	6.03	0.890	6.53	0.920	7.03	0.942	7.53
0.852	6.04	0.891	6.54	0.920	7.04	0.942	7.54
0.853	6.05	0.892	6.55	0.921	7.05	0.943	7.55
0.854	6.06	0.892	6.56	0.921	7.06	0.943	7.56
0.855	6.07	0.893	6.57	0.922	7.07	0.944	7.57
0.856	6.08	0.894	6.58	0.922	7.08	0.944	7.58
0.857	6.09	0.894	6.59	0.923	7.09	0.944	7.59
0.858	6.10	0.895	6.60	0.923	7.10	0.945	7.60
0.858	6.11	0.896	6.61	0.924	7.11	0.945	7.61
0.859	6.12	0.896	6.62	0.924	7.12	0.945	7.62
0.860	6.13	0.897	6.63	0.925	7.13	0.946	7.63
0.861	6.14	0.897	6.64	0.925	7.14	0.946	7.64
0.862	6.15	0.898	6.65	0.926	7.15	0.946	7.65
0.863	6.16	0.899	6.66	0.926	7.16	0.947	7.66
0.863	6.17	0.899	6.67	0.927	7.17	0.947	7.67
0.864	6.18	0.900	6.68	0.927	7.18	0.948	7.68
0.865	6.19	0.901	6.69	0.928	7.19	0.948	7.69

TABLE A.1 (CONTINUED)

$w(x)$	x	$w(x)$	x	$w(x)$	x	$w(x)$	x
0.866	6.20	0.901	6.70	0.928	7.20	0.948	7.70
0.867	6.21	0.902	6.71	0.929	7.21	0.949	7.71
0.867	6.22	0.902	6.72	0.929	7.22	0.949	7.72
0.868	6.23	0.903	6.73	0.930	7.23	0.949	7.73
0.869	6.24	0.904	6.74	0.930	7.24	0.950	7.74
0.870	6.25	0.904	6.75	0.930	7.25	0.950	7.75
0.871	6.26	0.905	6.76	0.931	7.26	0.950	7.76
0.871	6.27	0.905	6.77	0.931	7.27	0.951	7.77
0.872	6.28	0.906	6.78	0.932	7.28	0.951	7.78
0.873	6.29	0.907	6.79	0.932	7.29	0.951	7.79
0.874	6.30	0.907	6.80	0.933	7.30	0.952	7.80
0.874	6.31	0.908	6.81	0.933	7.31	0.952	7.81
0.875	6.32	0.908	6.82	0.934	7.32	0.952	7.82
0.876	6.33	0.909	6.83	0.934	7.33	0.953	7.83
0.877	6.34	0.910	6.84	0.934	7.34	0.953	7.84
0.877	6.35	0.910	6.85	0.935	7.35	0.953	7.85
0.878	6.36	0.911	6.86	0.935	7.36	0.953	7.86
0.879	6.37	0.911	6.87	0.936	7.37	0.954	7.87
0.880	6.38	0.912	6.88	0.936	7.38	0.954	7.88
0.880	6.39	0.912	6.89	0.936	7.39	0.954	7.89
0.881	6.40	0.913	6.90	0.937	7.40	0.955	7.90
0.882	6.41	0.913	6.91	0.937	7.41	0.955	7.91
0.883	6.42	0.914	6.92	0.938	7.42	0.955	7.92
0.883	6.43	0.915	6.93	0.938	7.43	0.956	7.93
0.884	6.44	0.915	6.94	0.939	7.44	0.956	7.94
0.885	6.45	0.916	6.95	0.939	7.45	0.956	7.95
0.885	6.46	0.916	6.96	0.939	7.46	0.957	7.96
0.886	6.47	0.917	6.97	0.940	7.47	0.957	7.97
0.887	6.48	0.917	6.98	0.940	7.48	0.957	7.98
0.888	6.49	0.918	6.99	0.941	7.49	0.957	7.99
0.888	6.50	0.918	7.00	0.941	7.50	0.958	8.00
0.958	8.01	0.970	8.51	0.979	9.01	0.985	9.51
0.958	8.02	0.970	8.52	0.979	9.02	0.985	9.52
0.959	8.03	0.971	8.53	0.979	9.03	0.986	9.53
0.959	8.04	0.971	8.54	0.979	9.04	0.986	9.54
0.959	8.05	0.971	8.55	0.980	9.05	0.986	9.55
0.959	8.06	0.971	8.56	0.980	9.06	0.986	9.56
0.960	8.07	0.971	8.57	0.980	9.07	0.986	9.57
0.960	8.08	0.972	8.58	0.980	9.08	0.986	9.58
0.960	8.09	0.972	8.59	0.980	9.09	0.986	9.59
0.960	8.10	0.972	8.60	0.980	9.10	0.986	9.60
0.961	8.11	0.972	8.61	0.980	9.11	0.986	9.61
0.961	8.12	0.972	8.62	0.981	9.12	0.986	9.62
0.961	8.13	0.973	8.63	0.981	9.13	0.987	9.63
0.962	8.14	0.973	8.64	0.981	9.14	0.987	9.64
0.962	8.15	0.973	8.65	0.981	9.15	0.987	9.65
0.962	8.16	0.973	8.66	0.981	9.16	0.987	9.66
0.962	8.17	0.973	8.67	0.981	9.17	0.987	9.67
0.963	8.18	0.973	8.68	0.981	9.18	0.987	9.68
0.963	8.19	0.974	8.69	0.982	9.19	0.987	9.69

TABLE A.1 (CONTINUED)

$w(x)$	x	$w(x)$	x	$w(x)$	x	$w(x)$	x
0.963	8.20	0.974	8.70	0.982	9.20	0.987	9.70
0.963	8.21	0.974	8.71	0.982	9.21	0.987	9.71
0.964	8.22	0.974	8.72	0.982	9.22	0.987	9.72
0.964	8.23	0.974	8.73	0.982	9.23	0.987	9.73
0.964	8.24	0.975	8.74	0.982	9.24	0.988	9.74
0.964	8.25	0.975	8.75	0.982	9.25	0.988	9.75
0.965	8.26	0.975	8.76	0.982	9.26	0.988	9.76
0.965	8.27	0.975	8.77	0.983	9.27	0.988	9.77
0.965	8.28	0.975	8.78	0.983	9.28	0.988	9.78
0.965	8.29	0.975	8.79	0.983	9.29	0.988	9.79
0.966	8.30	0.976	8.80	0.983	9.30	0.988	9.80
0.966	8.31	0.976	8.81	0.983	9.31	0.988	9.81
0.966	8.32	0.976	8.82	0.983	9.32	0.988	9.82
0.966	8.33	0.976	8.83	0.983	9.33	0.988	9.83
0.966	8.34	0.976	8.84	0.983	9.34	0.988	9.84
0.967	8.35	0.976	8.85	0.984	9.35	0.989	9.85
0.967	8.36	0.977	8.86	0.984	9.36	0.989	9.86
0.967	8.37	0.977	8.87	0.984	9.37	0.989	9.87
0.967	8.38	0.977	8.88	0.984	9.38	0.989	9.88
0.968	8.39	0.977	8.89	0.984	9.39	0.989	9.89
0.968	8.40	0.977	8.90	0.984	9.40	0.989	9.90
0.968	8.41	0.977	8.91	0.984	9.41	0.989	9.91
0.968	8.42	0.978	8.92	0.984	9.42	0.989	9.92
0.968	8.43	0.978	8.93	0.984	9.43	0.989	9.93
0.969	8.44	0.978	8.94	0.985	9.44	0.989	9.94
0.969	8.45	0.978	8.95	0.985	9.45	0.989	9.95
0.969	8.46	0.978	8.96	0.985	9.46	0.989	9.96
0.969	8.47	0.978	8.97	0.985	9.47	0.989	9.97
0.970	8.48	0.979	8.98	0.985	9.48	0.990	9.98
0.970	8.49	0.979	8.99	0.985	9.49	0.990	9.99
0.970	8.50	0.979	9.00	0.985	9.50		

PROBLEMS

The following representative problems are taken from the material presented in Chapters 2–5, 7, and 8. The answers to selected problems are included so that they may be of value in reinforcing the material to the researcher as well as the student.

2 Particle Distributions

2.1 Given the normal distribution function

$$f(L) = [1/\sigma(2\pi)^{1/2}] \exp[-(L - \bar{L})^2/2\sigma^2]$$

prove that the parameter σ satisfies the definition

$$\sigma^2 = \int_{-\infty}^{\infty} (L - \bar{L})^2 f(L) dL$$

and that the parameter $\bar{L}$ satisfies the definition of mean size

$$\bar{L} = \int_{-\infty}^{\infty} L f(L) dL$$

- 2.2 Show that the normal and log-normal distributions are normalized over their respective axes, i.e.,

$$\int_{-\infty}^{\infty} f(L) dL = 1$$

and

$$\int_{L=0}^{L=\infty} f(\log L) d(\log L) = 1$$

- 2.3 Show that the truncated log-normal distribution of Eq. (2.2-7) is normalized over the axis $\log[(L - L_1)/(L_2 - L)]$ in the interval L in (L_1, L_2) .
- 2.4 A gamma distribution of the form in Example 2.2-1 represents the distributive weight-size distribution of crystals from a steady-state mixed suspension crystallizer. If the mode size b is $300 \mu\text{m}$, find the average size $\bar{L}$ and the median size $\bar{L}_{50}$ of the distribution.
- 2.5 Calculate the skewness and kurtosis of the gamma-type CSD described in Problem 2.4.
- 2.6 Calculate the parameters $(\bar{L}, \sigma)$, $(\bar{L}', \sigma')$, and (a, b) and plot the normal, log-normal, and gamma distributions for an experimental particle weight-size distribution which has a mode of $500 \mu\text{m}$ and has 90% of its mass less than $800 \mu\text{m}$. Calculate the coefficient of variation predicted by each of these three distributions. Calculate the size below which 99% of the distribution is predicted to occur using these three distributions.
- 2.7 A gamma population distribution having a c.v. of 35.3% has a median size $\bar{L}_{50}$ of $600 \mu\text{m}$. Calculate the area-weighted mean size $\bar{L}_{3,2}$.

3 The Population Balance

- 3.1 Show that the dynamic one-dimensional population balance given as

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial L} (Gn) + \frac{n}{\tau} = 0$$

satisfies the general hyperbolic form

$$A \frac{\partial^2 n}{\partial t^2} + 2B \frac{\partial^2 n}{\partial L \partial t} + C \frac{\partial^2 n}{\partial L^2} = F\left(t, L, n, \frac{\partial n}{\partial t}, \frac{\partial n}{\partial L}\right)$$

where $B^2 - AC > 0$.

- 3.2 Simplify the macroscopic population balance for two equal-volume, mixed suspension cooling crystallizers operating in series. Assume different, but constant conditions in each vessel, i.e., $G_1 \tau \neq G_2 \tau$. Laplace-transform to obtain a single second-order transform describing population density in the second vessel in terms of G_1 , G_2 , n_1^0 , and n_2^0 .
- 3.3 Solve Problem 3.2 for $n_2(L)$ in terms of G_1 , G_2 , n_1^0 , and n_2^0 . What simplification in this form of CSD results when $G_1 = G_2$ and $n_2^0 = 0$? Express this simplified form as a dimensionless equation $y = y(x)$, where $y_2 = n_2/n_1^0$ and $x = L/G\tau$. Plot this dimensionless distribution and identify it with one of the distributions discussed in Chapter 2.
- 3.4 Write the macro-moment population balance for a steady-state, mixed suspension crystallizer to obtain an algebraic recursion relationship for the $(j-1)$ th and j th moments. Show that the exponential distribution $n = n^0 \exp(-L/G\tau)$ generates moments which satisfy this recursion relation.
- 3.5 Recognizing that the Laguerre polynomial is orthogonal on the interval $(0, \infty)$ with respect to the gamma-distribution weighting function, develop an orthogonal expansion of an arbitrary distribution $f(L)$ in terms of its Laguerre polynomial expansion without trying to constrain the first three moments to agree with the moments of $f(L)$. The coefficients in this expansion will again be a function of the moments $\{m_j\}$. Test the expansion by recovering the log-normal distribution described in Example 3.8-1.

4 The Steady-State MSMPR Crystallizer

- 4.1 Calculate the coefficient of variation of the population, length, area, and mass distributions of the ideal MSMPR crystal-size distribution.
- 4.2 An experimental CSD from a MSMPR crystallizer has a mass-averaged size $\bar{L}_{4,3}$ of 500 μm . The crystallizer operates with a suspension holdup of 800 gal and has a slurry discharge rate of 10 gpm. Calculate the linear crystal growth rate in microns/minute. If the suspension density is 0.15 gm crystals/cc of slurry and the product of the shape factor and the crystal density is 2.5 gm/cc, calculate density of nuclei and nucleation rate, number/cc-micron and number/cc-min, respectively.
- [Ans. $G = 1.56 \mu\text{m}/\text{min}$, $n^0 = 41$ nuclei/cc- μm , $B^0 = 64$ nuclei/cc-min.]
- 4.3 A crystal product obtained from a MSMPR crystallizer has an average size $\bar{L}_{1,0}$ of 600 μm . The crystals are cubic in habit and have a specific

gravity of 2.00. The suspension density is 200 gm/liter of crystallizer volume. The crystallizer has a working volume of 1000 gal and the slurry discharge rate is 10 gal/min. Calculate the crystal growth rate G (microns/minute) and the nucleation rate B^0 (number/liter-minute).

[Ans. $G = 6 \mu\text{m}/\text{min}$.]

- 4.4 When the crystallizer described in Problem 4.3 was operated with a concentration change δC of 100 gm/liter and a residence time of 200 min, the dominant particle size was 700 μm . When the residence time was changed to 50 min, the dominant particle size was 300 μm . Calculate and compare the growth and nucleation rates for each case. Comment on the character of the kinetics of nucleation and growth as they relate to supersaturation. Qualitatively discuss these relationships in the context of the feedback relationship shown in Fig. 4.5-1.

[Ans. $G_1 = 1.17 \mu\text{m}/\text{min}$, $B_1^0 = 3.27 \times 10^3$ nuclei/liter-min, $G_2 = 2.00 \mu\text{m}/\text{min}$, $B_2^0 = 1.67 \times 10^5$ nuclei/liter-min.]

5 The Unsteady State

- 5.1 Write out the transient moment equations for a Class I system in a MSMPR cooling crystallizer of volume V . Close the set by adding appropriate side and initial conditions. Assume system kinetics are given by

$$G = k_g(C - C_s) \quad \text{micron/minute}$$

$$B^0 = k_N(C - C_s)^i \quad \text{number/minute-volume slurry}$$

and the system is fed with flow rate Q and concentration C_i . What is the highest moment that has to be calculated to close the set? (Note: Nucleation kinetics are given on a slurry basis. Thus, the moments can be written on a slurry basis and the $d(\log V)/dt$ term dropped.)

- 5.2 Write out the transient moment equations for a Class II system in a MSMPR cooling crystallizer of constant volume V . Assume system kinetics of the form

$$B^0 = k_N G^i \quad \text{number/minute-volume slurry}$$

with growth rate constraint

$$G = (K \delta C) / \left(\tau \int_0^\infty n L^2 dL \right)$$

where K is a constant, $\delta C = (Q_i/Q_o) C_i - C_s$, and $\tau = V/Q_o$. What is the highest moment that is necessary to close the set? Assuming that the solute resources δC are dynamically varied, what is the highest moment that must be included to calculate transient production rate from the dynamic moments? Write an alternate differential equation to calculate transient production rate directly. This equation would serve as a check on the moment equations.

- 5.3 Assume the Class II system of Problem 5.2 with secondary nucleation kinetics given as

$$B^0 = k_N G^i m_1^j$$

and all system inputs invariant in time.

- (a) Make the set of moment equations dimensionless with the transformation

$$\theta = t/\tau, \quad y_j = m_j(\theta)/(m_j)_0, \quad \rho = G/G_o$$

utilizing the steady-state recursion relationship

$$(m_j)_0 = jG_o \tau (m_{j-1})_0$$

- (b) Linearize this set of dimensionless moment equations about the steady-state operating conditions $(y_j)_0 = \rho_0 = 1$.

- (c) Transform and write the characteristic equation of this linearized transformed set.

$$[Ans. \quad s^3 + 4s^2 + (6-j)s + (3+i-2j) = 0.]$$

- (d) Apply the Routh stability criterion to this characteristic equation to obtain a CSD stability criterion in terms of the parameters i and j .

$$[Ans. \quad i + 2j < 21.]$$

- 5.4 Repeat Problem 5.3 with secondary nucleation kinetics of the form

$$B^0 = k_N G^i m_4^j$$

Compare stability criteria in this and the previous problem with the criterion ($j=0$) given in Chapter 5, namely $i < 21$. Which kinetic expression gives the most limited stability region?

$$[Ans. \quad 5.4(c) \quad s^4 + 5s^3 + 10s^2 + (9+i)s + (3+i+j) = 0. \quad Ans. \quad 5.4(d) \quad i^2 - 7i + 25j < 294.]$$

7 Effects of Formation and Growth Kinetics on Particle-Size Distribution

- 7.1 A crystal system with a size-dependent growth rate of the form $G = G_0(1 + aL)$ is being produced in an MSMPR crystallizer. Using the steady-state equation for the third moment, show that $a < 0.333/G_0\tau$ is a necessary restriction to achieve a stable CSD having a finite third moment.
- 7.2 Droplet breakup in a dispersed-phase liquid–liquid system is given by $D(L) = kn(L)L^4$. Each drop breaks into three new liquid droplets of mass $\frac{1}{2}$, $\frac{1}{4}$, and $\frac{1}{4}$ of the original mass, respectively. Phrase a consistent birth function for this system $B(L)$ (neglecting coalescence) which conserves total droplet mass.
- 7.3 (a) The following nucleation–growth kinetics apply for a crystallization system: $B^0 = kG$. Show that at the same rate of make in an MSMPR crystallizer, a change in holding time alone will not change the size distribution.
- (b) Show the effect of a fourfold change of holding time on a system which exhibits fourth-order kinetics ($i = 4$). Compare with the effect of a fourfold change in holding time on a system which exhibits negative-order kinetics (e.g., $i = -2$).
- 7.4 Show that the two kinetic models proposed below give the same result when comparing size distributions obtained at two different rates of make. Take the holding time in the two cases to be equal.

$$B^0 = kM_T^j G^i$$

$$B^0 = kA_T^j G^i$$

It is clear from this example that the simple MSMPR crystallizer cannot be used to determine the exact mechanism of secondary nucleation.

8 Variations in Residence-Time Distributions

- 8.1 Fines dissolution is initiated in a Class II system having secondary nucleation kinetics of the form

$$B^0 = k_N G^4 M_T^{0.5}$$

Fines are removed at a size L_F small compared to product size at a rate

Q_F such that the dissolution parameter λ is

$$\lambda = Q_F L_F / G\tau = 4.3$$

Estimate the maximum expected size improvement measured as ratio of dominant size in product after and before initiation of fines dissolution.

- 8.2 Calculate the zeroth, first, and second moments of the weight distributions given by Eqs. (8.4-4)–(8.4-6) for the R - z CSD model with fines removal only (i.e., with $z = 1$) as a function of the dissolution parameter R and size of dissolution $x_1 = L_F / G\tau$. Calculate c.v. of the distribution as a function of x_1 and R . (Note: Product and crystallizer distributions are identical.)
- 8.3 Repeat Problem 8.2 with product classification but no dissolution (i.e., $R = 1$) as a function of the classification parameter z and classification size $x_2 = L_p / G\tau$. Calculate c.v. of the product and crystallizer distributions as a function of z and x_2 .
- 8.4 Show that fines dissolution is less effective as the order of nucleation increases. Explain the result qualitatively.
- 8.5 Solve the equation for size distribution from a batch evaporative system when the heat load is held constant. Assume growth rate is not a function of size and that nucleation rate is not a function of suspension density. Assume a single-size size distribution for an initial condition.

SOLUTION OF THE POPULATION BALANCE FOR SIZE DISTRIBUTION

The dimensionless set of equations representing the size distribution of a well-stirred, unseeded, continuous crystallizer are

$$\frac{\partial y}{\partial \theta} + \rho \frac{\partial y}{\partial x} + \frac{y}{\tau} = 0 \quad (\text{C.1})$$

$$\rho = \sigma/\tau f_2, \quad y^0 = \rho^{i-1}, \quad y_0 = \exp(-x)$$

when the nucleation rate is not a function of the solids in suspension (see Section 5.3). The normalized moments are

$$\begin{aligned} (df_0/d\theta) + (f_0/\tau) &= (\sigma/\tau f_2)^i \\ (df_1/d\theta) + (f_1/\tau) &= f_0 \sigma/\tau f_2 \\ (df_2/d\theta) + (f_2/\tau) &= f_1 \sigma/\tau f_2 \\ (df_3/d\theta) + (f_3/\tau) &= \sigma/\tau \end{aligned} \quad (\text{C.2})$$

The set (C.1) can be solved by the method of characteristics to give

$$\begin{aligned} y_1 &= [\exp(-\theta/\tau)] [y^0(\theta') \exp(-\theta'/\tau)]_{\theta'=\psi^{-1}[\psi(\theta)-x]}, & x < \psi(\theta) \\ y_2 &= [\exp(-\theta/\tau)] [y_0(x')]_{x'=[x-\psi(\theta)]}, & x > \psi(\theta) \end{aligned} \quad (\text{C.3})$$

where $\psi(\theta)$ is defined as

$$\psi(\theta) = \int_0^\theta \rho(p) dp \quad (\text{C.4})$$

The inverse notation $\theta' = \psi^{-1}(\psi(\theta) - x)$ is understood to mean that θ'_1 is the value of θ which satisfies $\psi(\theta'_1) = K$ for $\psi(\theta_1) - x = K$.

Equations (C.3) can be evaluated with the aid of the solutions to the moment equations (C.2) for upsets in rate of make σ or residence time τ . The following example illustrates the procedures.

EXAMPLE C.1

Calculate the transient response of dimensionless size $x = 1$ to a reduction in residence time to $\frac{1}{3}$ the original residence time for a system of nucleation order $i = 2$.

1. Solve set (C.2), Eq. (C.4), and $\rho = \sigma/\tau f_2$ simultaneously with an analog computer to get plots (a), (b), and (c) of Fig. C.1. For this computation, $i = 2$, $\sigma = 1$, and $\tau = \frac{1}{3}$. The initial conditions are all 1.

2. Prepare a plot of the initial size distribution in the crystallizer [Fig. C.1(d)].

3. (a) At time θ_1 , find $\psi(\theta_1)$ from Fig. C.1(c). If $x = 1 < \psi(\theta_1)$ find θ'_1 from this figure and evaluate the number density y_1 using θ_1 , θ'_1 , $\tau = \frac{1}{3}$, and $i = 2$. $y^0(\theta'_1) = [\rho(\theta'_1)]^{i-1}$. This gives the number density of crystals of size 1 at time θ_1 . (b) If $x = 1 > \psi(\theta_2)$, find $x' = 1 - \psi(\theta_2)$ and from Fig. C.1(d), find $y_0(x')$ as shown. Evaluate the number density with the equation for y_2 using θ_2 , $\tau = \frac{1}{3}$, and $y^0(x')$.

4. Repeat for all values of θ and x to get the complete transient response of the size distribution.

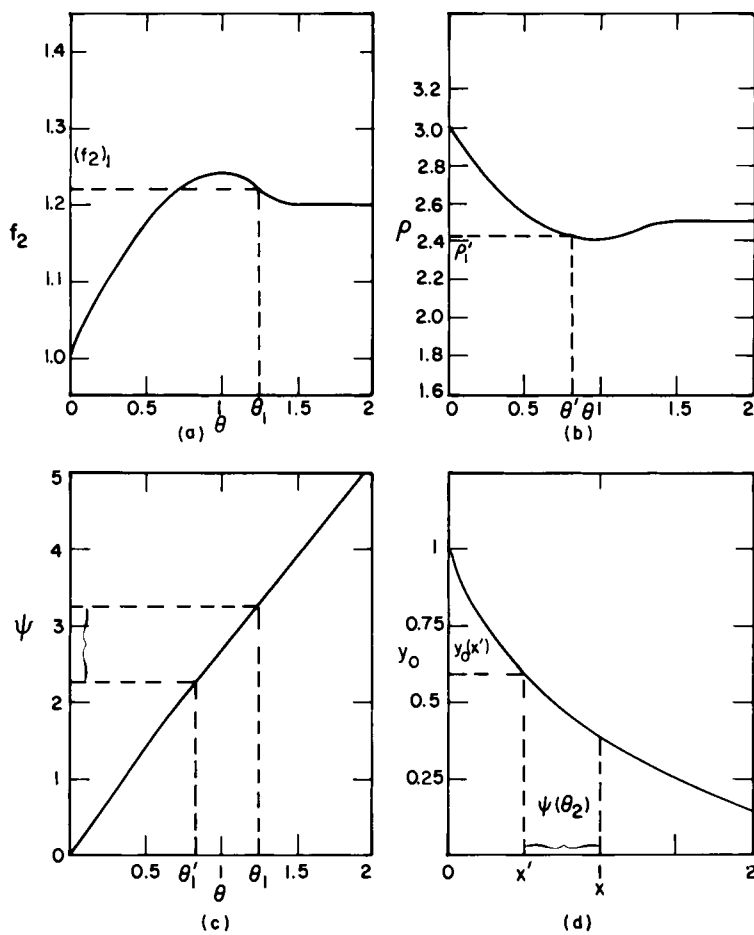


Fig. C.1 Plots for the solution of the dynamic population balance.

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